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ORGDP FUEL REPROCESSING STUDIES  
SUMMARY PROGRESS REPORT  
JANUARY THROUGH JUNE, 1967

## AUTHORS:

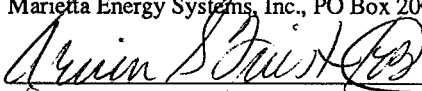
J. H. Pashley  
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Dwp #807

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Document: # K-1738 ; Date 5/9/68  
Title/Subject ORGDP FUEL REPROCESSING STUDIES SUMMARY  
PROGRESS REPORT, JANUARY THROUGH JUNE, 1967,  
by Pashley & Schappell

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Report K-1738

ORGDP FUEL REPROCESSING STUDIES  
SUMMARY PROGRESS REPORT  
JANUARY THROUGH JUNE, 1967

J. H. Pashley  
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Oak Ridge Gaseous Diffusion Plant  
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Nuclear Division  
Oak Ridge, Tennessee

Report Date: May 9, 1968

Report Classification: Unclassified

The Oak Ridge Gaseous Diffusion Plant Gaseous Diffusion Development Division is participating in studies of a group of processes aimed at purifying and recovering valuable uranium and plutonium from spent nuclear reactor fuels. The program includes two main phases: (a) preparation of conceptual plant studies with concomitant definition of problem areas associated with the process and technology and plant design; and (b) component development, including scale-up and testing of crucial process equipment and auxiliaries. The current report is the fifth in a series of progress reports to be issued semiannually. The topics covered include (1) the status of the current low-enrichment fuel flow sheet studies, including the systems analysis project and conceptual plant studies; (2) computation of properties of irradiated fuels; (3) effects of contamination of plutonium product with ruthenium; (4) criticality calculations; (5) semiworks interhalogen recycle system design; (6) process and reactor studies, including semiworks plant operation and bench-scale elutriation tests; (7) sampling experiments; (8) outlet gas filter studies; (9) connector evaluation; (10) uranium purification in a sorption-desorption system employing sodium fluoride; (11) testing of the ORGDP designed peripheral compressor; and (12) fluorination of Argonne National Laboratory reactor bed material for use in the Oak Ridge National Laboratory waste treatment experiments.

The report is 101 pages long and contains 12 figures and 28 tables.

Date of Issue: May 9, 1968

Report Number: K-1738

Subject Category: CHEMICAL SEPARATIONS  
PROCESSES FOR PLUTONIUM AND URANIUM

ORGD P FUEL REPROCESSING STUDIES  
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JANUARY THROUGH JUNE, 1967

J. H. Pashley  
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NUCLEAR DIVISION  
Oak Ridge Gaseous Diffusion Plant  
Oak Ridge, Tennessee



A B S T R A C T

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ORGBP FUEL REPROCESSING STUDIES  
SUMMARY PROGRESS REPORT  
JANUARY THROUGH JUNE, 1967

This report is the fifth in the series of semiannual summaries of Oak Ridge Gaseous Diffusion Plant work in the U. S. Atomic Energy Commission-sponsored volatility process development effort. The work has been performed in conjunction with development programs at Argonne National Laboratory and Oak Ridge National Laboratory. The ORGBP program has supported and extended the national laboratory efforts in two ways. First, conceptual plant studies leading to statement of technology problem areas, program analysis, and economic comparisons of alternative flow sheets have been performed. Second, a component development program has been conducted to cover scale-up and testing of crucial process equipment and auxiliaries. Perhaps the most significant item has been the semiworks fluid-bed reactor system to provide scale-up data for the main (head-end) fluid-bed reactor.

Emphasis has continued to be placed on the study of low-enrichment power reactor fuel reprocessing systems. Reporting will continue to be on a semiannual basis but, as substantive completion is achieved in various areas, topical reports will be issued.

SUMMARY

ENGINEERING STUDIES

LOW ENRICHMENT FUELS

Engineering studies were focused on the bromine pentafluoride fluorination process and included work on the conceptual full-scale processing plant, systems analysis, plutonium criticality computations, and adaptation of the semiworks plant for the interhalogen process.

In addition, because ruthenium is the key component in the plutonium purification scheme, computations of radiation dosages from plutonium and from ruthenium-contaminated plutonium were made in a project exploring the possibility that the current decontamination goals might be reduced.

Systems Analysis

The systems analysis format has been revised for the interhalogen fluorination scheme, and the original question-answer scheme has been retained. A compendium of 440 questions has been prepared covering all processing steps except plutonium hexafluoride separation and plutonium product purification. About 260 problem statements, i.e., answers, have been written.

### Conceptual Plant Studies

The size of the standard fuel charge to be fed to the conceptual 1 MTU/day plant has been chosen based on current and near-future thermal power reactor fuel assembly designs. The irradiated charge would contain about 1,277 kg of 0.98% uranium-235 enriched uranium and 12.4 kg of plutonium, the major part of which would be the plutonium-239 isotope.

When a plant reactor is loaded with a standard fuel cycle and fluid-bed diluent alumina which is in use for a fifth processing cycle, all 190,000 Btu/hr of alpha and beta energy and 90.3% of the 123,000 Btu/hr of gamma energy emitted by the retained fission products will be dissipated within the reactor. The reactor must, therefore, be designed to remove about 301,000 Btu/hr of radioactive heat, as well as the heat of chemical reaction.

The bromine pentafluoride regenerator has been sized assuming that reaction kinetics are rapid, and thus, gas components are present in equilibrium concentrations at any point in the reactor. The estimated heat load is about 500,000 Btu/hr for 99% conversion of the bromine to bromine pentafluoride. About 165 square feet of cooling surface is required for the air-cooled reactor. The flame temperature would be about 1030°C. To limit the overall length of the vessel, the wall would be equipped with both internal and external fins. The gases from the regenerator would be further cooled to about 100°C before cold trapping of the bromine pentafluoride-uranium hexafluoride. For this cooler, 180 square feet would be provided in an air-cooled unit similar to the regenerator.

Two cold trapping systems are required with interhalogen fluorination. One system, the primary, is to remove the bulk of the uranium hexafluoride and bromine pentafluoride from the full 125 scfm process gas stream. Four equally sized traps would be provided, with three of them to be used in parallel to handle the full flow. Operation would be at minus 50°C. Each trap would be 15 inches in inside diameter, 5 feet long, and would contain sufficient fins to obtain a heat transfer surface of about 450 square feet. The secondary system would handle about one-third of the gas stream from the primary trapping system. A single trap operating at about minus 90°C would be used. This trap should be about 7 feet long with a heat transfer area of about 225 square feet.

Uranium hexafluoride collected in the cold traps will contain bromine pentafluoride and possibly some bromine trifluoride. Distillative separation has been demonstrated to give relatively low bromine trifluoride and bromine pentafluoride levels in uranium hexafluoride. A few parts per million of either interhalogen would be enough to force the uranium hexafluoride product off the specification limit (5 parts bromine per million parts of uranium). While fluorine might be fed into the column to retard internal formation of bromine trifluoride because of corrosive reactions, the step may not be fully effective, especially if the column feed contains much bromine trifluoride. In order to achieve specification grade uranium hexafluoride, a series of two batch columns would be provided, allowing the separation of bromine pentafluoride from uranium

hexafluoride in the first and bromine trifluoride from uranium hexafluoride in the second. Both columns would be of bubble-plate design, sized for a 1-day batch distillation cycle time. The first column would be 14 inches in inside diameter and would contain 58 trays spaced 8 inches apart; uranium hexafluoride would collect in the reboiler. The second column would be 7-1/2 inches in inside diameter and would contain 55 trays on a 6-inch spacing. The uranium hexafluoride would leave as overhead product from the latter column. The low and high boiling fission products would, in all likelihood, be removed if bromine halide specifications are met; nevertheless, product polishing sorbent traps would also be provided.

Sections entitled (1) Bases for Study, (2) Process Technology, (3) Process Description, (4) General Facilities, and (5) Safety have been completed in rough draft form for the conceptual plant report. Chapters on Process Critique and Costs were in preparation. A total cell floor area of 4,500 square feet was planned. Equipment placement was made on the basis that a track-mounted manipulator was available for remote maintenance at the bottom of the head-end processing cells, and an overhead manipulator mounted on a crane bridge will be available at the top of the cells.

#### Composition of Irradiated Fuels

A formal report is in preparation on the SFP computer code, developed at ORGDP, for the estimation of the properties of irradiated reactor fuel. The code was used recently to supply estimates of fission product and heavy element inventories in irradiated Yankee reactor fuel pellets.

#### Contamination of Plutonium with Ruthenium

The current specifications for fission product activity in plutonium product necessitate decontamination factors for ruthenium during volatility processing as high as  $2.6 \times 10^6$ . Ruthenium appears to be the key fission product in the plutonium purification scheme, and even a relatively modest change in the specification might be of considerable benefit to the volatility process.

Calculations were made of the dose rates for ruthenium and from power reactor produced plutonium and its decay products. A fuel burnup of 25,000 Mwd/tonne of uranium and a cooling period of 120 days were assumed. Based on the gamma dose rate from ruthenium and the gamma and neutron dose rates from plutonium and its daughter products, a factor of about  $5 \times 10^4$  for ruthenium decontamination would reduce the total dose from that source to a level equivalent to that from the plutonium, assuming a short period of aging after recovery before use in fuel fabrication.

#### Criticality Calculations

Plutonium, rather than uranium, is the controlling factor in criticality considerations for low-enrichment irradiated fuel volatility reprocessing systems. The effects of alumina dilution on the critical radius of infinite cylinders containing plutonium dioxide powder and on the critical mass of a sphere containing plutonium dioxide powder were computed. As

the concentration of plutonium dioxide (density of 3.2 g/cc) is decreased from 100 to 20 volume percent, the calculated critical radius of an infinite cylinder increases from 7.85 to 30.08 cm, and the critical spherical mass increases from 42.4 to 113.7 kg of plutonium.

In addition, the critical radii and the effective multiplication factors for infinitely long cylinders reflected with reinforced phenolic foam were computed in a study of the use of the foam as an insulator for a plutonium hexafluoride cold trap. The critical radii varied from 11.5 to 11.09 cm for reflector thicknesses of 0 to 12 cm, respectively.

Hanford plutonium nitrate critical data were used to check the accuracy of the plutonium cross-sections used in the ANISN computer code. The computed effective multiplication factors were, for the most part, within 1% of criticality for the stated assemblies.

#### Semiworks Interhalogen Plant Design

Preliminary drawings were made covering system layout, equipment, instrumentation, and piping.

The regenerator size chosen was 6 inches in diameter and 16 feet long. The total heat load was computed to be about 44,000 Btu/hr; however, internal fins or packing are not needed.

A batch distillation column, 4 inches in inside diameter by 15 feet tall was selected for the purification of the uranium hexafluoride from the interhalogen-uranium hexafluoride condensate-desublimates collected in the cold trap. High efficiency 0.24-inch Cannon packing is to be used, and stage heights of 5 and 10 inches have been assumed where the mole fraction of bromine pentafluoride was above and below 0.001, respectively. The column would be charged and refluxed for several hours until steady state is reached. At that point, withdrawal of bromine pentafluoride would be initiated. The uranium hexafluoride would be retained in the column for discharge when specification purity is attained. If bromine trifluoride formation cannot be controlled through the use of a small stream of fluorine during distillation, the uranium hexafluoride in the column will be redistilled in the same column, taking the uranium hexafluoride off the top and leaving the bromine trifluoride in the reboiler.

#### PROTOTYPE TESTING AND EVALUATION

The projects undertaken during the report period covered the decladding, oxidation, and fluorination phases of the volatility process.

#### PROCESS AND REACTOR STUDIES

Additional semiworks tests have been completed involving oxidation, chemical decladding, and fluorination with elemental fluorine. In support of the reactor test program, bench-scale elutriation and fluidization

experiments were conducted using reactor bed material from early semi-works oxidation runs.

#### Semiworks Plant

Sixteen new runs have been conducted involving individual oxidation and fluorination tests or combinations of decladding, oxidation, and fluorination. Zircaloy tubing was reacted in most of the declad tests. EGCR type annular cylindrical pellets were employed in the oxidation tests. The reactor beds from oxidation runs UE-17 and -21 were used in two fluorination tests using elemental fluorine.

Interest was centered in particular on the operating conditions for chemical decladding with hydrogen chloride and the elutriation of  $U_3O_8$  fines from the reactor bed during oxidation. The fluorination tests were designed primarily as scoping studies, since hardware capability for use of bromine pentafluoride, the current flow sheet reagent for uranium fluorination, was not available.

The tests indicated the following:

1. A decladding run can be controlled successfully using stepwise increased concentrations of hydrogen chloride.
2. The permeability of nickel filters decreases markedly upon exposure to the declad reaction off-gases.
3. During EGCR pellet oxidation, a minimum superficial gas velocity must be maintained. For shallow pellet beds (up to about 1 foot deep), this velocity is 1 ft/sec, while between 2 and 3 ft/sec is satisfactory for deeper beds. Due to the greater voidage of the reacting beds of pellets, the annular EGCR pellets can probably be oxidized at lower velocities than smaller solid cylindrical pellets.
4. The elutriation of  $U_3O_8$  during oxidation in the semiworks plant is higher when preceded by the declad step than when conducted alone. In the latter case, 12 to 32% of the uranium charge has been elutriated as compared to 55 to 94% in two-step runs.
5. Large amounts of  $U_3O_8$  are elutriated unreacted from a fluidized bed during fluorination with elemental fluorine. Since the same effect may be expected with bromine pentafluoride, it appears that provisions must be made to return the material to the bed or a secondary reactor must be located below the off-gas filter.

#### Bench-Scale Elutriation and Fluidization Studies

Tests were conducted in a 7-1/2-foot-long, 2-inch-diameter Plexiglas column to investigate the elutriation properties of the  $U_3O_8$  product of the semiworks fluid-bed oxidation step. The two charge material batches used contained 19 and 76%  $U_3O_8$  in alumina.

When the lower concentration charge was tested at velocities of from 1.0 to 2.5 ft/sec, 91 to 92% of the  $U_3O_8$  was elutriated; with the high concentration charge, 87 to 96% of the  $U_3O_8$  was elutriated. The test data indicate the existence of an apparent minimum  $U_3O_8$  bed concentration which possibly may be nonelutriatable. A bed velocity of about 2 ft/sec may be optimal for elutriation of this material.

#### SAMPLING

Additional sampling tests were conducted in the 6-inch Denver Vezin solids sampler. The feeds contained 27.6 and 70%  $U_3O_8$  in tabular alumina, and the feed rate was varied from about 400 to 8,000 lb/hr.

The sampler data showed that an average sample cut of 5 to 5.5 weight percent was obtained in all runs. A comparison of the true mean  $U_3O_8$  concentration versus the statistical data based on chemical analysis of the samples indicated that the equipment takes representative samples with little or no bias.

#### OUTLET GAS FILTER STUDIES

An additional eleven exposure tests were conducted in the filter test loop. In one test, a porous Inconel tubular filter was checked for suitability with the zircaloy declad and oxidation phases of the process cycle. In the remaining tests, the sintered nickel fiber filter tubes manufactured by Huyck Metals Company were subjected to various treatments in a program to explore the loss of permeability during exposure to de-cladding reaction off-gases. While most of the latter tests were conducted with a single tube, there were two tests undertaken with two tubes in series.

In the test with the Inconel filter, the permeability loss after five cycles of exposure was 75%, which is lower than that experienced with the sintered nickel filter tubes exposed under similar conditions. The comparison may be poor because of the greater original porosity of the Inconel unit.

The nickel filters plugged as much as 94% during the tests with the zircaloy decladding off-gases and 85% with zirconium substituted for the alloy. The test with zirconium will be continued.

In the two-filter-in-series tests, the secondary filter plugged sufficiently to indicate that at least one volatile species is involved in the loss of permeability rather than reactor bed material powders.

The tests also revealed that a separate hydrogen treatment after decladding at temperatures as low as 315°C is effective in decreasing the plugging. On the other hand, the presence of excess hydrogen in the declad off-gas does not prevent plug formation.

### CONNECTORS

It was concluded that Inconel-X might be more desirable as a bolt material for flanges in the ORNL fluoride volatility processing plant than steel, chiefly because Inconel was not expected to rust at high operating temperatures.

### PRODUCT PURIFICATION SORPTION-DESORPTION SYSTEM

Studies with nitrogen vapors containing 2 to 3.7% uranium hexafluoride have been made in the 4-inch-diameter sodium fluoride sorption test loop at superficial gas velocities of 1 ft/sec. Outlet uranium hexafluoride concentrations during sorption were less than 50 ppm until breakthrough. The sorption ratios (0.18 to 0.34 pounds of uranium hexafluoride per pound of sodium fluoride at breakthrough) were similar to those in tests with 10% uranium hexafluoride.

### PERIPHERAL COMPRESSOR

An inspection of all components after the first long-term operation test found evidences of fluorine attack only at the forward and rear ball bearing retainer rings. These retainer rings are made of a phenolic type material which probably suffered damage early in the test when there was an insufficient supply of nitrogen to the shaft seal. The buffer system has since been reworked to prevent reoccurrence of the difficulty.

The compressor was reassembled and extended-period testing has been resumed. To date, 1,293 hours has been logged.

### FLUORINATION OF ANL REACTOR BED MATERIAL

Nonirradiated volatility process reactor bed material from Argonne National Laboratory runs BRF5-5 through -8 have been fluorinated with elemental fluorine at 550°C and a superficial gas velocity of 0.5 ft/sec.

ANL had requested 50% fluorine in nitrogen to be used. A temperature excursion after 50% fluorine was added to run BRF5-5 material and bed caking after run BRF5-6 was fluorinated indicated that the bromine pentafluoride exposures had failed to satisfy the fluorine demand in these cases. Runs BRF5-7 and -8 were first fluorinated with low concentrations of fluorine; no temperature excursions developed, and very little bed caking was observed.



## DISCUSSION

ENGINEERING STUDIES

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LOW ENRICHMENT FUELS

Since the adoption of the interhalogen reference flow sheet, the scope of the engineering work has been shifted from comparison of the competitive fluorine and bromine pentafluoride fluorination schemes to a concentrated effort on the interhalogen conceptual plant study. The systems analysis effort has correspondingly been revised to cover the interhalogen reference flow sheet. During the current report period, in addition to this work, several related projects were continued or initiated including plutonium criticality calculations, evaluation of the influence of incomplete removal of ruthenium or radiating problems associated with power reactor-produced plutonium, estimation of fission product content of irradiated Yankee fuel, and semiworks plant redesign for the interhalogen process.

Systems Analysis

The systems analysis program functions as a major aid in highlighting process areas for concentrated study and in evaluating alternate process routes within the framework of the reference flow sheet.

The original program has been restructured for the bromine pentafluoride-fluorine (interhalogen) flow sheet along the lines of the matrix-type format illustrated in figure 1. Each block in the grid represents an area in which a number of problems exist. Discussions of these problems are prepared on a question-and-answer basis, similar to that used in the first systems analysis effort.

A compendium of 440 questions has been prepared covering all processing steps except plutonium hexafluoride separation and plutonium product purification. The preparation of questions for these steps must be held up, pending additional laboratory studies and the adoption of suitable flow sheets.

About 260 answer write-ups have now been prepared for the Main Fluid-Bed Reactor, Reactor Off-Gas Cooling and Filtration, the Pyrohydrolysis Fluid Bed, Hydrogen Chloride Recovery, Bromine Pentafluoride Recovery, the Uranium Hexafluoride Separation Systems, and for areas of overall interest, such as bromine pentafluoride safety and general ventilation.

PROCESS SYSTEM	TYPE OF PROBLEM					
	OPERATION	PROCESS	DESIGN	SAFETY	CONSTRUCTION	ACCOUNTABILITY
I MAIN FLUID-BED REACTOR CHARGING						
DECLAD						
OXIDATION						
INTERHALOGEN FLUORINATION						
FLUORINE FLUORINATION						
BED DUMPING AND SAMPLING						
II REACTOR OFF-GAS COOLING AND FILTRATION						
III PYROHYDROLYSIS FLUID BED						
IV HCl RECOVERY SYSTEM						
V BrF <sub>5</sub> FEEDING, REGENERATION, RECYCLE, AND HANDLING SYSTEM						
VI UF <sub>6</sub> SEPARATION COLD TRAPPING AND DISTILLATION						
VII PuF <sub>6</sub> SEPARATION COLD TRAPPING AND FLUORINE RECYCLE						
VIII PLUTONIUM PRODUCT PREPARATION						
IX GENERAL						

SYSTEMS ANALYSIS GRID

Figure 1

### Conceptual Plant Studies

Conceptual plant studies for the interhalogen reference flow sheet were continued for both the single- and the two-vessel main reactor system schemes. The work will continue in an engineering feasibility report for a volatility plant with a processing rate equivalent to a 1 MTU/day throughput.

The plant flow scheme is, in essence, as follows:

The zircaloy cladding is removed by treatment with anhydrous hydrogen chloride, the then-exposed dense uranium dioxide ceramic fuel is oxidized with oxygen to form a bed of finely divided  $U_3O_8$  powder, the uranium is volatilized as uranium hexafluoride by fluorination with bromine pentafluoride vapor, and then the plutonium is volatilized as plutonium hexafluoride by contact with concentrated elemental fluorine. These reactions take place consecutively in a single fluidized bed reactor. The volatility approach has then been used to separate the uranium and plutonium from the charge and from each other.

Auxiliary process operations include steam hydrolysis of the metal chloride off-gases during decladding to form nonvolatile solid waste and hydrogen chloride vapor; the regeneration of bromine pentafluoride from uranium fluorination off-gases; separation of the uranium hexafluoride from its regenerated fluorinating agent and subsequent uranium hexafluoride purification; plutonium collection and purification; and the separate recycling of hydrogen chloride, bromine pentafluoride, and fluorine-containing streams.

Much of the equipment for the plant has been sized; conceptual design drawings have been prepared; and the engineering report has been started. Since suitable volatility process procedures for plutonium purification have, however, not been developed at the national laboratories, it has been necessary to make allowances for costs, space requirements, and necessary auxiliaries. Although these appear fairly reasonable even if aqueous purification\* were required, considerable revision could be necessary when process details are firmer.

Highlights of the conceptual plant study are detailed in the subsections which follow:

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\* Ruthenium is apparently the key fission product in the plutonium purification scheme with an overall decontamination factor of about  $10^6$  apparently required to meet specifications. The maximum decontamination factor achieved thus far in ANL tests has been on the order of only  $10^2$ . Computations are being made to compare dose rates from aged plutonium and from aged plutonium-ruthenium mixtures to explore the possibility of liberalization of the specification.

Main Fluid-Bed Reactor. Reactor sizing has been discussed in the previous report\*. A preliminary time cycle for the main fluid-bed reactor for a single vessel process is now presented in table I. With the total cycle time of 54 hours and two reactor lines, the cyclic plant processing rate is 1.14 MTU/day. Since it is felt that time allotments for the individual reaction steps may be a little conservative, it appears that the assumption of a nominal 1 MTU/day throughput rate is certainly reasonable with this sizing.

TABLE I

## PRELIMINARY ESTIMATES OF MAIN FLUID-BED REACTOR TIME CYCLES

Step	Time, hr
Charge	1
Hydrochlorination	12
Purge	1
Oxidation	14
Bromine Pentafluoride Fluorination	8
Purge	1
Fluorine Fluorination	15
Purge	1
Transfer Bed	<u>1</u>
	54

Cyclic Uranium Processing Rate, 0.57 MTU/day/line.

The expected standard fuel charge has been selected based on current and near-future thermal power reactor fuel assemblies. The size of the standard fuel charge is approximately equivalent to three Westinghouse, seven General Electric, or three Combustion Engineering elements. Typical fuel assembly and fuel rod dimensions for the vendors are given in table II. These data are based on recent hazards analysis report. Compositions and activity values for the standard charge are given in table III

\* Smiley, S. H., Pashley, J. H., and Schappel, R. B., ORGDP Fuel Reprocessing Studies Summary Progress Report July through December, 1966, Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, June 12, 1967 (K-1717), p. 25.

TABLE II  
TYPICAL FUEL ASSEMBLY AND FUEL ROD DIMENSIONS

	<u>Westinghouse</u>	<u>General Electric</u>	<u>Combustion Engineering</u>
<u>Fuel Assemblies</u>			
Rod Pattern	15 × 15	7 × 7	15 × 15
Number of Fuel Rods	204	49	217
Number of Other Rods	21	none	8
Rod Pitch, inch	0.563	0.738	0.553
Nominal Distance Between Adjacent Rods, inch	0.141	0.170	0.140
Cross-Section, inch	8.43 × 8.43	5.438 × 5.438	8.16 × 8.16
Probable Cut Length, inch	150	160	142
Can	Canless	Removable	Canless
<u>Intermediate Grids</u>			
Type	Eggcrate	Eggcrate	Eggcrate
Overall Dimensions, inch	8.45 × 8.45 × 2	5.45 × 5.45 × 2	8.18 × 8.18 × 2
Thickness of Each Strip, inch	0.015	0.015	0.015
<u>Fuel Rods</u>			
Outside Diameter, inch	0.422	0.568	0.413
Clad Thickness, inch	0.0243	0.035	0.024
Diametral Gap, inch	0.0065	0.010	0.006
Fuel Length, inch	144	144	132
Gas Plenum Length, inch	6	16	6-3/4
Rod Length, inch	150	160	139

TABLE III

## ESTIMATED STANDARD CHARGE FUEL PROPERTIES\*

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<u>Initial Fuel Composition</u>	
Uranium-235, kg	36.36
Uranium-238, kg	1,285.86
Total Uranium, kg	1,322.22
Uranium-235 Assay, %	2.75
<u>Final Fuel Composition</u>	
Uranium-235, kg	12.54
Uranium-236, kg	4.42
Uranium-238, kg	1,259.85
Total Uranium, kg	1,276.81
Uranium-235 Enrichment, %	0.98
Plutonium, kg	12.40
<u>Plutonium Isotopic Distribution</u>	
Plutonium-239, %	60.45
Plutonium-240, %	21.79
Plutonium-241, %	13.56
Plutonium-242, %	4.20
Total curies	5,417,000
Total Energy Release, Btu/hr	71,320

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\* Based on 24,755 Mwd/T irradiation at a specific power of 24.8 Mw/T and 120 days cooling time. The values were calculated using the SFP computer code developed at ORGDP.

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as calculated, using the SFP computer code developed at ORGDP\*. The standard irradiation fuel charge contains about 1,277 kg of uranium at a uranium-235 assay of 0.98%. The plutonium weight per charge is 12.4 kg.

The SFP code has been used to calculate the energy emitted by fission products present in the main fluid-bed reactor when loaded with a standard fuel charge together with alumina which has been used to process four previous standard fuel charges†. Virtually all of the energy due to alpha and beta radiation will be dissipated within the reactor, since the range of these particles is short in the fluid-bed material. A significant portion of the energy due to gamma radiation, however, will pass out of the reactor, since these particles are uncharged and have relatively long ranges. The gamma fraction that escapes the main reactor has now been estimated.

The average density of the fluid-bed mixture was assumed to be 100 lb/cu ft, and the reactor was assumed to be a two-diameter vessel with an 18-inch-diameter lower section and a 26-inch-diameter upper section. Based on bed depths of 12 and 6 feet in the larger and smaller diameter regions, respectively, the mean radius of the bed would be 11.67 inches. The SDC code\*\* calculated the average gamma flux at the surface of the reactor vessel to be  $1.946 \times 10^{11}$  gamma/sq cm-sec. There is a large amount of high energy gamma in the gamma distribution spectrum. Based on an energy weighted surface flux, 9.7% of the gamma energy emitted escapes from the reactor.

Details of the computations are listed by mode of decay in table IV. Based on the data presented, the reactor cooling system must be designed for removal of about 300,000 Btu/hr of radioactive heat, as well as for the heat of chemical reaction.

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\* Merriman, J. R., Estimation of Irradiated Reactor Fuel Properties for Reprocessing Studies, M. S. Thesis, University of Tennessee (December, 1966); and K-1717, loc cit., pp. 32-35.

† The recycle alumina contains the fission products that are not volatilized during the various process steps.

\*\* Arnold, E. D., and Maskewitz, B. F., SDC, A Shielding-Design Calculation Code for Fuel Handling Facilities, Union Carbide Corporation, Nuclear Division, Oak Ridge National Laboratory, March, 1966 (ORNL-3041).

TABLE IV  
FLUID-BED RADIOACTIVE HEAT LOAD  
DURING FIFTH RECYCLE USAGE OF ALUMINA

<u>Mode of Decay</u>	<u>Fission Product Energy Emitted, Btu/hr</u>	<u>Fission Product Energy Dissipated in the Reactor, Btu/hr</u>
Alpha	7,028	7,028
Beta	183,167	183,167
Gamma	<u>123,019</u>	<u>111,086</u>
Total	316,214	301,281

Regenerator Design. The reactions relative to the regeneration of bromine pentafluoride are expected to proceed in a manner similar to a flame with the kinetics of the reaction being fast enough so that, at any point, the components are present in equilibrium concentrations. Provided that this flame-equilibrium model is reasonably valid, the required size of the regeneration vessel can be estimated based on heat transfer considerations alone.

For a reprocessing plant with a maximum on-stream uranium hexafluoride production rate of about 460 kg/hr\*, the heat load for the regenerator is on the order of 500,000 Btu/hr for 99% conversion of the bromine to bromine pentafluoride. Equilibrium computations indicated that the adiabatic flame temperature would be about 1030°C in the initial gas contacting zone of the regenerator and that the reacting gases would have to be cooled to about 430°C to achieve greater than 99% conversion of the bromine in the feed to the wanted pentafluoride. Results obtained from heat

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\* This is equivalent to a cyclic rate of about 7.5 MTU/day which is, of course, substantially higher than the nominal 1 MTU/day plant throughput. There are two reasons for this apparent disparity, both connected with the batch processing nature of the current plant concept. First, the bromine pentafluoride reaction time is only about 12% of the cycle time for a one-vessel batch reactor line. Thus, considering that there are two reactor lines serviced by the regenerator, that unit is only on-line slightly over 25% of the time. Secondly, there is a tail-off period at the end of the fluorination with bromine pentafluoride, such that considerably less than maximum reaction occurs. This tail-off period occupies about 35% of the fluorination time. Obviously then, the regenerator design described here would service a considerably larger plant if continuous throughput could be maintained through the bromine pentafluoride fluorination operation.



transfer calculations for a single tube regenerator, jacketed for counter-current flow with cooling air, indicate that about 165 square feet of surface would be required to remove the 500,000 Btu/hr heat load based on the area exposed to the reacting gases. The resulting heat flux for the regenerator is on the order of about five times less than the heat flux for the main fluid-bed reactor. The lower heat fluxes result from differences in the heat transfer coefficients for the two modes of heat transfer; i.e., cooling of a fluid bed ordinarily results in much higher heat transfer coefficients than cooling of a gas stream.

The conceptual sketch of the regenerator is shown in figure 2. To limit the overall length of the vessel, both internal and external fins would be attached to the regenerator wall for additional cooling surface. The tube would be bisected lengthwise for attachment of the internal fins and then sealed for completion of the fabrication. The fins are slotted to increase gas-phase heat transfer coefficients.

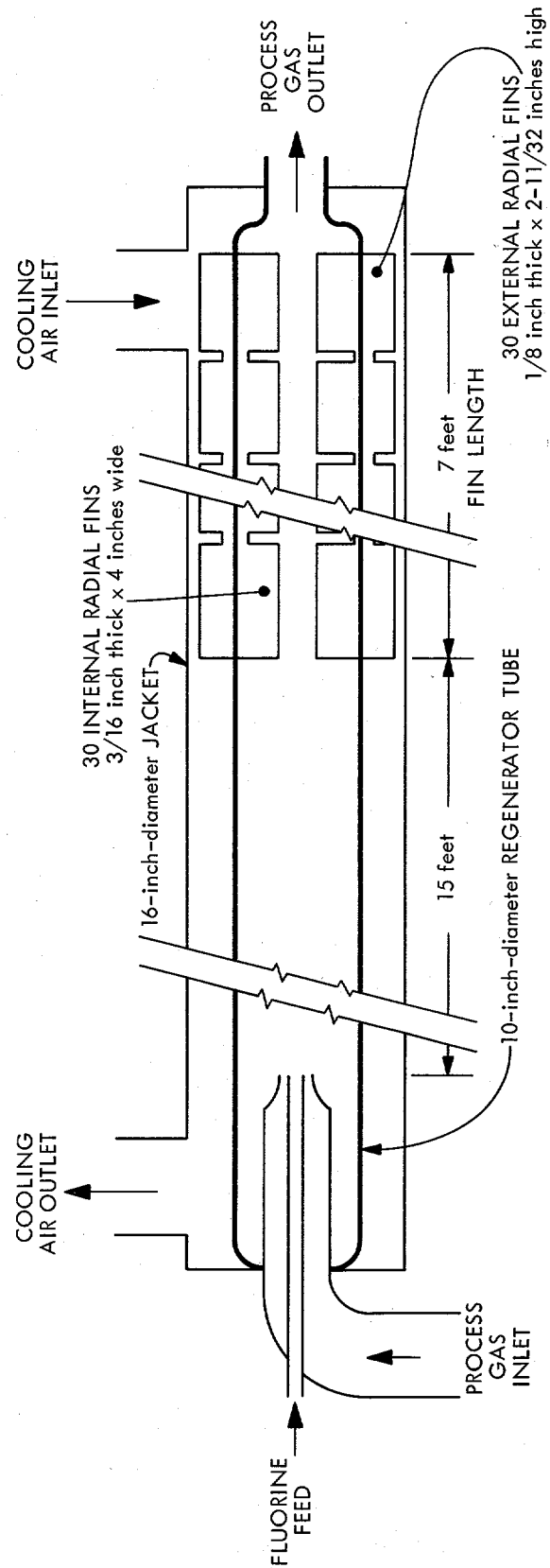
Gas Cooler Design. The temperature of the exhaust gases from the bromine pentafluoride regenerator will be about  $430^{\circ}\text{C}$ . Before these gases can be fed to the cold trapping operation, it is necessary to cool them to about  $100^{\circ}\text{C}$  so that the heat transfer capacity of the cold traps can be used most efficiently. The temperature of the exhaust gases from the regenerator may be lowered using a single tube cooler, jacketed for countercurrent air flow. To limit the overall length of the vessel, both internal and external fins can be attached to the wall of the internal tube for extra cooling surface. The heat loading is computed to be about 125,000 Btu/hr.

The cooler is similar in design to the regenerator. An effective internal heat transfer area of about 180 square feet has been provided based on an 80% fin efficiency. This area is somewhat in excess of the theoretical requirement but allows for uncertainties in heat generation, as well as inlet temperature of the gas coming from the bromine pentafluoride regenerator.

Design of Cold Trapping Systems. Two cold trapping systems are required with interhalogen fluorination in the bromine pentafluoride volatility reprocessing plant. The primary system, operating at minus  $50^{\circ}\text{C}$ , cools the full gas stream (about 125 scfm) from the fluorination reactor and the bromine pentafluoride regenerator and removes the bulk of the uranium hexafluoride (about 15 scfm) as solid and bromine pentafluoride (about 18 scfm) as liquid condensate. About one-third of the gas stream leaving the primary trapping system is vented to a secondary cold trap, operating at minus  $90^{\circ}\text{C}$ , where most of the remaining bromine pentafluoride and uranium hexafluoride are collected as solid before the vent gas stream is sent to off-gas treatment facilities.

Since the trapping system would represent a major investment in the plant, it would be important to reduce the capital cost of the equipment. For the conceptual plant primary system, a set of four identical traps to be operated in parallel is provided, with three of them to be capable of handling the complete process cycle if one should be out of service. Design calculations indicate that each trap should be 15 inches in inside

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PLANT-SCALE BROMINE PENTAFLUORIDE REGENERATOR

Figure 2

diameter. Radial fins which are provided for heat transfer surface allow for drainage of the liquid phases. At the trap inlet, twenty such fins are arranged in the annular space between the shell and the 5-inch-diameter center pipe which carries the exit gases from the trap. The number of fins increases stepwise in subsequent portions of the vessel until seventy are provided at the gas exit end. Fin height is, at most, 5 inches, allowing heat transfer efficiencies of about 80%. The complete trap has a length of about 25 feet, and a total heat transfer surface of about 450 square feet. Although the trap design is such that plugging should not occur during a normal processing cycle, fins near the gas inlet extend only 4 inches in from the trap wall, providing an annular section for gas flow around the relatively warmer center pipe should plugging tend to occur at some point in this part of the trap.

The secondary trap is, for design purposes, essentially a gas cooler, since only about 30 kg of solid is expected to be collected during a cycle, as opposed to 1,900 kg in the primary system. A single trap, similar to a primary trap with 70 radial fins throughout, has been designed for this service. This trap should be about 7 feet long with a heat transfer area of about 225 square feet and will collect about 99% of the condensables reaching it.

Uranium Hexafluoride-Bromine Halide Separation. Uranium hexafluoride collected in the cold trapping system during the interhalogen fluorination will contain bromine pentafluoride and, in addition, some bromine trifluoride that either has not been fully converted during the bromine pentafluoride regeneration or has been formed during corrosion reactions in process equipment. Bromine itself should not be present; the reaction with bromine pentafluoride should be fast enough to convert any that is formed in process equipment to bromine trifluoride.

Distillative separation of bromine pentafluoride and bromine trifluoride from uranium hexafluoride is difficult since the relative volatilities of bromine pentafluoride to uranium hexafluoride and of uranium hexafluoride to bromine trifluoride are both close to one. At high uranium hexafluoride concentrations, the region of primary interest, the relative volatility of bromine pentafluoride to uranium hexafluoride is about 1.8\* and of uranium hexafluoride to bromine trifluoride, 1.3†. Distillative separations,

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\* Liimatainen, R. C., Vapor-Liquid Equilibrium in the System Bromine Pentafluoride-Uranium Hexafluoride, Argonne National Laboratory, May, 1959 (ANL-6003).

† Estimated from data found in: Fischer, J., and Vogel, R. C., Phase Equilibria in the Condensed System Bromine Trifluoride-Uranium Hexafluoride, Argonne National Laboratory, November 8, 1953 (ANL-5130), pp. 12-15; Maslan, F., Progress Report Nuclear Engineering Department February 15 through December 31, 1965, Brookhaven National Laboratory (BNL-434[S-34]), p. 13; and Page, W. R., Raseman, C. J., Goodman, E. I., and Scarlett, C. H., A Continuous Flow Pilot Plant for the Separation of Bromine-Fluorine Compounds and Light End Fission Product Fluorides from Uranium Hexafluoride, Brookhaven National Laboratory, March, 1952 (BNL-174).

however, have been demonstrated to the 1 ppm\* and 1,000 ppm† bromine levels for bromine pentafluoride and bromine trifluoride, respectively. In the latter case, no attempt was actually made to reach a 1 ppm bromine as bromine trifluoride levels‡. Thus, distillative separation appears feasible. The primary consideration is, then, the arrangement of the distillation system.

In the above-mentioned demonstration of uranium hexafluoride-bromine pentafluoride distillation, a stream of fluorine was bled into the column to avoid problems of bromine trifluoride within the still itself; the formation of a few parts per million bromine trifluoride from corrosion reactions within the column would be, of course, enough to force the product off specification. The action of the fluorine in the column is a matter of conjecture, however, and in the absence of more complete data, it would appear that the reaction of bromine trifluoride and fluorine under column conditions might be slow enough that, if a significant amount of bromine trifluoride were already in the column feed, it might not be satisfactorily removed through reaction. The presence of small amounts of less volatile bromine trifluoride also has the effect of decreasing the apparent column stage efficiency in removing bromine compounds by a factor of at least two\*. For these reasons, it appears that facilities for both uranium hexafluoride-bromine pentafluoride and uranium hexafluoride-bromine trifluoride separations should be provided\*\*. The concurrent removal of low and high boiling fission products appears to be readily accomplished if bromine halide removal specifications are met; nevertheless, further product purification of the still products is allowed for by provision of sorbent traps in the conceptual plant.

Several alternative distillation systems were analyzed. Of these, the three most promising were found to be (1) a series of two continuous columns, the bottom product of the first being fed to the second, with bromine pentafluoride being withdrawn from the top of the first and bromine trifluoride from the bottom of the second; (2) a series of two batch columns, allowing the separation of bromine pentafluoride from uranium hexafluoride in the first and bromine trifluoride from uranium

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\* Long, R. D., Martin, J. J., and Vogel, R. C., "Liquid-Vapor Equilibria of the System Bromine Trifluoride-Bromine Pentafluoride", I & EC, 3 (1), 28-34.

† BNL-174, loc cit.

‡ The current AEC specification on bromine content in uranium hexafluoride is 5 ppm on a uranium weight basis (30, No. 232, F. R. 14938 [December 2, 1956] and 30, No. 230, F. R. 14821).

\*\* The bromine trifluoride problem is also discussed in the write-up for the uranium hexafluoride-bromine pentafluoride still under the semi-works plant design (pages 50 to 54). Tests in a semiworks column would determine the magnitude of the problem and a treatment satisfactory to attain purified product.

hexafluoride in the second; and (3) a single batch column from which uranium hexafluoride would be withdrawn as a side stream during the course of a run. A system of taking cuts from a single batch column was also analyzed but was discarded because the high reflux ratio that would have to be used between the bromine pentafluoride and uranium hexafluoride cuts would require either a rather large column or extremely long operating times.

Calculations for the continuous system indicated that the first column would require 60 to 70 theoretical stages, and the second about 20, with some variation possible, of course, depending upon operating conditions. The system of two batch columns, which would utilize approximately equivalent column flow rates, would require about 35 theoretical stages for the first column and about 30 for the second. Thus, the two-column batch system would be somewhat smaller than the continuous system and, in addition, because the stages per column are more nearly equally distributed, would probably result in a considerably reduced building height requirement with consequent cost savings. Analysis of various batch column schemes showed that the key problem involves the cut between bromine pentafluoride and uranium hexafluoride. If bromine pentafluoride is to be completely removed from the column in the distillate, excessively long operating times are required. The single batch column with side stream was proposed as a solution to this problem but was found to require a large number of theoretical stages (about 100) and a high reflux ratio during uranium hexafluoride removal. As with the continuous system, the large number of stages required in the single batch column would probably lead to excessive column height and resultant increased building costs.

The most satisfactory scheme that has been analyzed uses one batch column to remove bromine pentafluoride until the material in the first still reboiler meets specifications as far as bromine concentration due to this compound is concerned. The contents of this reboiler are then transferred to a second still, while the first still is refluxed to keep bromine pentafluoride in the column. Uranium hexafluoride is then removed as overhead product from the second still. Since both columns may be maintained refluxed between charging cycles, start-up times may be kept to a minimum. The system of two batch columns should also be the most adaptable to cleanup operations involving treatment of process inventories and heels between processing campaigns.

Stage height is a key factor in this design, since a relatively large number of theoretical equilibrium stages (about forty) are required for each column, and there are practical limitations to cell headroom and column pressure drop. High efficiency packings tend to give low stage heights but, to attain this, characteristically have shapes using high surface area-to-volume ratios. In the column environment, this could lead to increased corrosion and a resultant deterioration of packing efficiency over extended periods of time. Ultimately, the choice of column internals was between plate column designs and packings deemed to be more able to withstand corrosion. It was estimated that somewhat smaller stage heights could be achieved with bubble plates than with the more conventional packings. A sieve tray unit might be considered but apparently

would require impractically small sieve holes to provide a reasonable operating range. Thus, bubble plate design was chosen for this application.

Column efficiency was predicted both from a generalized overall tray efficiency versus viscosity-relative volatility correlation\* and from published comparisons with the standard n-heptane-methylcyclohexane system†, coupled with efficiency data for that system‡. Both methods lead to an overall efficiency of about 60%. The latter method was used directly to obtain a Murphree plate efficiency from which the overall efficiency was then determined for this work.

The columns were sized for flow rates using the same method as for the semiworks distillation column and checked with a computer code which was also used to determine the number of theoretical and actual stages required. The results of the design calculations are summarized in table V. Sufficient capacity is provided to handle the flows from the conceptual plant with a 1-day column cycle time.

TABLE V  
COLUMN DESIGN PARAMETERS

	UF <sub>6</sub> -BrF <sub>5</sub> Distillation Column	UF <sub>6</sub> -BrF <sub>3</sub> Distillation Column
Column Inside Diameter, inches	14	7.5
Bubble Cap Outside Diameter, inches	2	1.5
Number of Caps per Tray	10	3
Tray Spacing, inches	8	6
Number of Trays	58	55
Approximate Overall Pressure Drop, atmosphere	0.5	0.5

\* Perry, J. H., Ed., Chemical Engineers' Handbook, 4th Edition, pp. 18-17, McGraw-Hill, New York (1963). The correlation is shown in graphical form in figure 18-29.

† Ivins, R. O., The Distillation of Uranium Hexafluoride and Bromine Pentafluoride in a 0.5-Inch Diameter Packed Column, Argonne National Laboratory, May, 1962 (ANL-6362).

‡ Perry, J. H., loc cit., pp. 18-23.

Scrubber System. Four scrubbers are planned. In the first unit, probably a packed column, water will be used to scrub hydrogen chloride from a gas side stream vented from the hydrogen chloride recycle system during dechlorination. Since this gas also contains hydrogen, the stream must be kept separate from those containing oxidizing materials such as oxygen or bromine pentafluoride, at least until it is possible to dilute below the explosive limit. In a second column, both the process off-gases from the oxidation step and a side stream from the bromine pentafluoride recycle system will be scrubbed using a potassium hydroxide solution. This chemical has been found effective in neutralizing fluorides and fluorine, thus permitting the use of filters downstream of the scrubbers without attack on the filtering media.

The third scrubber is designed to handle the combined ventilation off-gases from the following cells; hydrogen chloride recycle, uranium hexafluoride product collection, the head end, fuel drying and handling, and bromine pentafluoride cycle. When the halide or radioactive contamination in the gas from these cells is acceptably low, the scrubber will be bypassed, and the flow will pass directly to a filtering system. Should these contaminants be detected, the ventilation gas would be directed into the scrubber for cleanup prior to passage through the filters. A venturi scrubber would probably be used for this application.

The fourth scrubber is to handle process and cell off-gases from the plutonium fluorination and purification facilities. A soluble poison would be added to the scrubber solution for criticality control purposes. A tray column using a potassium hydroxide solution would probably be employed. In passing through the unit, the process and cell off-gases would be humidified. Moisture hydrolyzes plutonium hexafluoride, and the plutonium can then be filtered out as a solid salt either in the scrubber system or the backup filters.

Cell Layouts. Equipment placement is being made on the basis that a track-mounted manipulator will be available for remote maintenance at the bottom of the cell, and an overhead manipulator mounted on a crane bridge will be available for remote maintenance at the top of the cell. The track-mounted manipulator will run down the middle of the head end, bromine pentafluoride, and scrubber cells, which are aligned end to end. The manipulator will be stored in the decontamination cell. To make it possible for the manipulator to travel through all these cells and to maintain control of ventilation air when the manipulator is not in use, ventilation doors are inserted in cell partition walls. Equipment removal will also be possible using a cart on the manipulator tracks. Tentatively, a total cell floor area of 4,500 square feet is planned. The individual process cell dimensions are given in table VI.

TABLE VI  
PROCESS CELL DIMENSIONS  
CONCEPTUAL VOLATILITY PROCESSING PLANT

Cell	Height, ft	Width, ft	Length, ft
Head-End Cell	37.5	16.5	24
Bromine Pentafluoride Recycle Cell	37.5	16.5	30
Fluorine Recycle Cell	18	16.5	17
Scrubber Cell	37.5	16.5	18.5
Hydrogen Chloride Recycle Cell	18	8	53.5
Uranium Purification Cell	18	8	39
Plutonium Purification Cell	20	9	21
Decontamination and Maintenance Cell	37.5	42.5	40
Fuel Drying and Handling Cell	18	7	25.5
Sampling Cubicles (3)	18	8	9

Report Preparation. Sections entitled (1) Bases for Study, (2) Process Technology, (3) Process Description, (4) General Facilities, and (5) Safety have been completed in rough draft form. Assumptions were made for the plutonium purification portion of the plant in matters involving space allocation, shielding, and costing. Throughout the study, complete conformity to AEC and Federal Safety Standards was assumed. The plant was considered to be required to be independent and self-sustaining for processing, waste disposal, utilities (except normal electrical supply), administration, warehousing, maintenance, and laboratory analytical work.

Housed in the plant's main building complex are processing cells; a control room; areas for administration, fuel receipt and handling, and maintenance; a laboratory; and decontamination facilities. Fuel receiving and handling facilities include a cask cleanup area, separate unloading and storage pools, and a cask decontamination pit. The process areas of high radio-activity are located in a canyon extending through the center of the process building and are maintained remotely by manipulators operating from overhead and floor-mounted conveying devices. Viewing is remote (by TV), and in some cases, lead glass windows are also used. The high-level solids waste generated during processing will be stored in underground annular storage bins located on the plant site.

Chapters entitled Process Critique and Costs are now in preparation. Detailed estimates of capital and operating charges will be developed in



the chapter on costs. Capital costs will include buildings, structures, facilities, land improvements, construction costs, engineering design, equipment, contingencies, and provisions for equipment spares and startup. Operating costs will include labor, materials, employee plans, depreciation, equipment replacement, overhead, and contingencies. On the other hand, the operating costs will not contain allowances for fuel transportation, special insurance, funding for perpetual care of wastes, interest on the capital investment, local taxes, profit, reserve for charges for uranium losses, and miscellaneous allocated charges from government agencies for contract administration, etc, or for credits for recoverable plant value after shutdown or from by-product sales.

#### Composition of Irradiated Fuels

A formal report is in preparation on the SFP computer code for the estimation of the properties of irradiated reactor fuel. The code was developed at ORGDP and has been discussed in previous reports.

The code was used to supply estimates of fission product and heavy element inventories in the irradiated Yankee reactor fuel pellets recently processed in ANL experiments. The pellets considered in these calculations were irradiated to a level of about 33 Mwd/kg of uranium. Table VII presents a summary of the values for selected isotopes in a 100-gram uranium dioxide sample after a one-year cooling period.

TABLE VII  
CONCENTRATION OF SELECTED NUCLIDES  
IN IRRADIATED (33 Mwd/kg URANIUM) YANKEE PELLETS

Nuclide	Estimated Amounts*	
	Curies	Grams
Krypton-85	0.700	0.00171
Ruthenium-106	17.5	0.00550
Cesium-137	9.58	0.0975
Strontium-90	5.91	0.0416
Cerium	26.1	0.208
Molybdenum	-	0.286
Uranium	-	84.1
Plutonium	17.3	1.06

\* Values are for 100-gram uranium dioxide samples irradiated and then cooled for one year.

### Contamination of Plutonium with Ruthenium

Calculations have been made to estimate the gamma and neutron dose rates from power reactor produced plutonium and its decay products and to compare these dose rates with the gamma dose rates of ruthenium in an evaluation of the possibility of relaxation of the current fairly rigid specification for fission products in plutonium. As stated previously, ruthenium is apparently the key fission product as far as plutonium decontamination is concerned. It was felt that the power reactor plutonium might have sufficient inherent activity that relaxation would be permissible without significant increase of the hazards of handling the material.

The isotopic composition of plutonium and ruthenium was obtained from the SFP code for fuel burned to 25,000 Mwd/tonne and cooled for 120 days. The amount of plutonium and ruthenium present after this burnup and cooling time is shown in table VIII for 1,500 kg initial weight of uranium dioxide.

TABLE VIII

#### ISOTOPIC COMPOSITION OF PLUTONIUM AND RUTHENIUM\*

<u>Isotope</u>	<u>Weight, g/1,500 kg initial uranium dioxide</u>
Plutonium-238**	186
Plutonium-239	7,380
Plutonium-240	2,660
Plutonium-241	1,650
Plutonium-242	510
Ruthenium-103	5.4
Ruthenium-106	130

\* Content in reactor fuel after 25,000 Mwd/tonne burnup and 120-day cooling prior to processing.

\*\* Estimated from Yankee core data. Yankee Core Evaluation Program, Quarterly Progress Report for the Period Ending June 30, 1966, Westinghouse Atomic Power Division, Pittsburgh, Pennsylvania, August, 1966 (WCAP-6081).

The Nuclear Fuels Services plutonium specifications state that the maximum permissible fission product gamma plus beta activity is 50 microcuries per gram of plutonium\*. The combined gamma plus beta activity from ruthenium and its decay products before reprocessing is about 128 curies per gram of plutonium based on the above burnup and cooling time. Dividing 128 curies by 50 microcuries would give a required decontamination factor of about  $2.6 \times 10^6$  for ruthenium, assuming ruthenium is the only fission product contaminant.

The activity of the plutonium after processing will come from the decay of the plutonium itself; from the decay of plutonium daughter products; e.g., americium-241 and uranium-237; and from the decay of ruthenium and its daughter products. The amount of each component present changes with time; therefore, the amount of each component present from 0 to 3 years after processing has been calculated using the appropriate decay schemes. For purposes of this study, the amount of each plutonium isotope present can be considered to be constant, since each has a relatively long half-life. The amounts of the other components in curies that change with time are shown in table IX. The amount of plutonium present in curies is shown in table X. From tables IX and X, it can be seen that the activity from ruthenium is substantially greater than that from plutonium and its decay products, americium-241 and uranium-237, for the first year.

TABLE IX

ACTIVITY OF DECAY PRODUCTS OF PLUTONIUM AND RUTHENIUM  
VERSUS TIME AFTER PROCESSING

Isotope	Activity at the Indicated Time After Processing, curie/gram plutonium				
	0 year	0.25 year	0.50 year	1 year	3 years
Americium-241	0	0.0059	0.0112	0.0224	0.0637
Uranium-237	0	0.0006	0.0006	0.0006	0.0005
Ruthenium-103	13.7	2.84	0.58	0.025	negligible
Rhodium-103M	13.7	2.84	0.58	0.025	negligible
Ruthenium-106	35.4	29.8	25.1	17.7	4.4
Rhodium-106M	<u>35.4</u>	<u>29.8</u>	<u>25.1</u>	<u>17.7</u>	<u>4.4</u>
Total	98.2	65.3	51.4	35.5	8.9

\* Hearing before the Joint Committee on Atomic Energy Congress of the United States, Eighty-Eighth Congress, First Session on Chemical Reprocessing Plant, U. S. Government Printing Office, Washington, D.C., May 14, 1963, p. 348.

TABLE X  
ACTIVITY OF PLUTONIUM AFTER PROCESSING

<u>Isotope</u>	<u>Activity, curies/gram plutonium</u>
Plutonium-238	0.254
Plutonium-239	0.037
Plutonium-240	0.048
Plutonium-241	15.3*
Plutonium-242	<u>negligible</u>
Total	15.6

\* This is mainly beta activity with a relatively low energy, i.e., 0.02 mev.

Plutonium-241, the major contributor to the plutonium total, decays almost exclusively by beta decay, while the isotopes of ruthenium and its decay products, with the exception of ruthenium-106, have high gamma yields. Furthermore, the energy of the emitted gamma is larger for ruthenium than for plutonium. For these reasons, it is evident that ruthenium and its decay products will be the major contributors to the total gamma dose.

The gamma dose rates from a 1 kg sphere of plutonium with the above components have been calculated at a point 3 feet from the sphere using the shielding design code (SDC). The results of these calculations are shown in table XI. The neutron dose rates from spontaneous fission and alpha-neutron reactions have been calculated for plutonium and americium at a point 3 feet from the source based on an average neutron energy of 0.75 mev and a 1 kg sphere of plutonium (as plutonium tetrafluoride), assuming no attenuation in air. The sphere density was taken as that of pure plutonium metal and both self-shielding and the neutron multiplication factor were neglected. The total neutron dose is shown in table XII. It should be pointed out that, of the isotopes shown in table XII, plutonium-239 would be the only major constituent in low burnup fuels. Plutonium-239 contributes less than 7% to the total neutron dose for the assumed high burnup case as shown in table XII. The neutron yields from spontaneous fission and alpha-neutron reactions were obtained from an ANL publication.

\* Steindler, M. H., Radiation Problems Associated with the Handling of the Actinide Elements, Argonne National Laboratory, April, 1962 (ANL-6540).

TABLE XI

## GAMMA DOSE RATES 3 FEET FROM 1 KG SPHERE OF PLUTONIUM

Isotope	Average Gamma Energy, mev	Gamma Dose Rates at the Indicated Time After Processing, mrem/hour/kg plutonium				
		0 year	0.25 year	0.5 year	1 year	3 years
Plutonium-238	0.100	0.0002	0.0002	0.0002	0.0002	0.0002
Plutonium-239	0.100	0.0001	0.0001	0.0001	0.0001	0.0001
Plutonium-240	0.100	0.00004	0.00004	0.00004	0.00004	0.00004
Plutonium-241	-	-	-	-	-	-
Plutonium-242	-	-	-	-	-	-
Americium-241	0.100	0.0	0.00003	0.00007	0.00013	0.00037
Uranium-237	0.180	-	0.8044	0.8005	0.7758	0.6977
Total		0.00034	0.8047	0.8008	0.7763	0.6983
Ruthenium-103, Rhodium-103M	0.234	326,000	67,700	11,300	596	-
Ruthenium-106, Rhodium-106M	0.87	<u>1,192,000</u>	<u>1,000,000</u>	<u>845,000</u>	<u>596,000</u>	<u>149,000</u>
Total from Ruthenium-Rhodium		1,518,000	1,067,700	856,300	596,596	149,000

TABLE XII

NEUTRON DOSES FROM PLUTONIUM AND AMERICIUM  
AT 3 FEET FROM SOURCE\*

Isotope	Dose at the Indicated Time After Processing, mrem/hr/kg plutonium				
	0 year	0.25 year	0.5 year	1 year	3 years
Plutonium-238	26.9	26.9	26.9	26.9	26.9
Plutonium-239	2.1	2.1	2.1	2.1	2.1
Plutonium-240	2.8	2.8	2.8	2.8	2.8
Plutonium-241	negligible	negligible	negligible	negligible	negligible
Plutonium-242	negligible	negligible	negligible	negligible	negligible
Americium-241	0.0	1.3	2.5	4.9	13.8
Total	31.8	33.1	34.3	36.7	45.6

\* Based on fuel burned to 25,000 Mwd/tonne and cooled for 120 days. Of the isotopes shown, only plutonium-239 would be present in significant quantities for low burnup fuels. It is assumed that the plutonium is present as plutonium tetrafluoride in a spherical assembly.

The relationship of the gamma dose rates from plutonium and its decay products compared to that of ruthenium can be seen from table XI. Decontamination factors for ruthenium in the range  $4.5 \times 10^9$  to  $2.1 \times 10^5$ , depending on cooling time, would be necessary to reduce the gamma dose to the level of that from the plutonium. It should be noted, however, that ruthenium derived gammas are substantially harder than those associated with plutonium.

The ruthenium gamma dose rate, including the dose from its rhodium daughter product, is also greater than the plutonium neutron dose rates by factors ranging approximately from  $5 \times 10^4$  to  $3 \times 10^3$  for 0 and 3 years after processing, respectively. Thus, based on the respective total dose rates from plutonium and ruthenium, a factor of about  $5 \times 10^4$  ruthenium decontamination would bring its total dose to a level equal to that of plutonium aged only a short time after recovery.

Although it might be desirable to consider much more specific situations involved in handling of plutonium in fuel fabrication, including the contrasting problems introduced by the neutron activity of the plutonium and the ruthenium-rhodium gamma, it appears from the preceding calculations that limited liberalization of the specification may be possible. Even a relatively modest change in the specification might be of considerable benefit to the volatility and perhaps the aqueous route also.

### Criticality Calculations

Plutonium, rather than uranium, is the controlling factor in criticality calculations for low enrichment, irradiated fuel processing systems. In striking contrast to the large amount of data published with respect to uranium, there is a decided dearth of information in the field of plutonium criticality.

Further studies were made on plutonium systems as an extension of the criticality computational work described in the previous semiannual progress report\*. The new calculations were made for plutonium dioxide-alumina systems and for a plutonium hexafluoride cold trap. In addition, another check of the DTF code was made by calculation of the effective multiplication factors for plutonium assemblies which had been experimentally determined to be critical.

Plutonium Dioxide-Alumina Mixtures. The effect of alumina dilution on the critical radius of infinite cylinders of plutonium dioxide and on the critical sphere mass of plutonium dioxide has been studied. Calculations were made for various homogeneous mixtures of plutonium dioxide and alumina at a plutonium density† of 3.2 g/cc and an alumina density of 2.5 g/cc. Reflection with 30 cm of alumina was assumed.

Diluting plutonium dioxide with alumina affects the critical dimensions in two ways. First, the presence of alumina increases the critical size and mass by reducing the density of the plutonium in the mixture. Second, the alumina partially compensates for the dilution by acting as a neutron moderator. Thus, the critical size and mass obtained with allowance for alumina dilution will be somewhat less than that obtained by simply reducing the plutonium dioxide density, with no diluting materials present.

The effect of alumina dilution on the critical radius of an infinitely long cylinder of plutonium dioxide is shown in table XIII. Table XIV shows the effect of alumina dilution on the critical sphere mass and compares these results with the mass obtained by simply reducing the plutonium dioxide density, with no diluting materials present.

Plutonium Hexafluoride Cold Trap. The plutonium hexafluoride cold trap will be insulated to prevent heat losses during operation. This insulation will act as a neutron reflector and will reduce the critical radius of a bare cylinder to a certain extent, depending on the nuclear properties of

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\* K-1717, loc cit., pp. 35-43.

† In this and other calculations reported here, unless otherwise stated, the plutonium was taken to be all as the plutonium-239 isotope. This assumption is conservative with respect to power reactor produced materials which contain considerable amounts of plutonium-240 and -242.

TABLE XIII

CRITICAL RADII OF INFINITE CYLINDERS  
OF PLUTONIUM DIOXIDE-ALUMINA HOMOGENEOUS MIXTURES\*

Plutonium Dioxide, volume percent	Plutonium Dioxide Density, g/cc	Critical Radius, cm
100	3.628	7.85
80	2.903	9.11
60	2.177	10.93
40	1.451	14.20
20	0.726	21.10
10	0.363	30.08

\* Reflected with 30 cm alumina. Alumina reflector and alumina diluent assumed to have density of 2.5 g/cc. Plutonium is all as plutonium-239 isotope.

TABLE XIV

CRITICAL MASS OF PLUTONIUM DIOXIDE-ALUMINA SPHERES\*

Plutonium Dioxide, volume percent	Plutonium Dioxide Density, g/cc	Critical Mass, kg plutonium	
		Plutonium Dioxide and Alumina Mixture	Plutonium Dioxide Only**
100	3.628	42.4	42.4
80	2.903	49.1	54.0
60	2.177	59.5	75.0
40	1.451	76.6	116.0
20	0.726	113.7	

\* Reflected with 30 cm alumina. Alumina reflector and diluent assumed to have density of 2.5 g/cc. Plutonium is all as the plutonium-239 isotope.

\*\* No diluting materials present. Values are interpolated from previous calculations.



the reflector. This effect can be minimized by choosing an insulation material that is a good neutron absorber, such as the reinforced phenolic foam developed on an engineering basis at ORGDP as a protective lining for fissile material containers\*.

Computations were made to evaluate this material in plutonium hexafluoride cold trap applications. The composition of this insulation is shown in table XV. Critical radii of infinitely long cylinders of plutonium hexafluoride reflected with varying thicknesses of the insulation are shown in table XVI based on a plutonium hexafluoride density of 6.0 g/cc at the minus 180°C operating temperature of the cold trap. Effective multiplication factors were then calculated for varying radii of infinitely long cylinders of plutonium hexafluoride with 10 cm of the reinforced phenolic foam as insulation. These calculations are shown in table XVII.

TABLE XV  
COMPOSITION OF REINFORCED PHENOLIC FOAM INSULATION

<u>Element</u>	<u>Weight Percent</u>	<u>Atom Density*, atoms/barn-cm</u>
Carbon	57.02	0.003203
Hydrogen	4.80	0.003236
Boron	3.08	0.0001919
Chlorine	3.92	0.0000745
Oxygen, Silicon, Fluorine	31.18	0.001313

\* Based on a density of 7 pounds per cubic foot. One barn is equal to  $10^{-24}$  square centimeters.

\* Union Carbide Corporation, Chemical Division, originally developed the foam which serves as the basic ingredient for the insulation. The work at ORGDP involved the choice of proper additives for increased structural strength and for correction of shrinking and cracking problems when the basic foam was subjected to temperatures above 120°C. For further information, refer to Mallet, A. J., and Wheatley, S. J., Fissile Material Container and Packaging Development and Testing Program, Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, April 1, 1966 (K-1661), pp. 17-34.

TABLE XVI

CRITICAL RADII OF INFINITE CYLINDERS OF PLUTONIUM HEXAFLUORIDE\*  
REFLECTED WITH VARYING THICKNESSES OF REINFORCED PHENOLIC FOAM\*\*

Reflector Thickness, cm	Critical Radius, cm
0	11.50
2	11.39
4	11.31
8	11.19
12	11.09

\* Plutonium hexafluoride density = 6.0 g/cc. Plutonium is all as the plutonium-239 isotope.

\*\* Reinforced phenolic foam density = 7.0 lb/cu ft.

TABLE XVII

$k_{eff}$  VERSUS RADIUS FOR INFINITE CYLINDERS OF PLUTONIUM HEXAFLUORIDE\*  
REFLECTED WITH REINFORCED PHENOLIC FOAM\*\*

Cylinder Radius, cm	$k_{eff}$
11.14†	1.0
10.0	0.899
8.0	0.717
6.0	0.529
4.0	0.342
2.0	0.164

\* Plutonium hexafluoride density assumed equal to 6.0 g/cc; reflector thickness equals 10 cm. Metal wall thickness is not included in the calculation.

\*\* Reinforced phenolic foam density equals 7.0 lb/cu ft.

† Extrapolated from data in table XVI.

The assumed 6.0 g/cc density for plutonium hexafluoride at minus 180°C is conservative, since it is estimated to be the crystal density at that temperature with no adjustment for voidage in the deposit.

ANISN Code Results Versus Critical Experiments. The ANISN Code\* has been used to make most of the plutonium criticality calculations for volatility processing of spent thermal power reactor fuels. The code has been found to give essentially the same results as its predecessor, the DTF code. Both codes are basically the same but the former contains several additional options.

A series of checks of ANISN code output versus plutonium criticality experimental results has been employed to evaluate the accuracy of the plutonium cross-sections used in the code. In each case, the critical size was used as input and an effective multiplication factor ( $k_{\text{eff}}$ ) calculation was made. Checks made using plutonium nitrate and plutonium dioxide-polystyrene data from the Hanford Laboratories and plutonium metal data from Los Alamos were reported previously†.

Additional Hanford plutonium nitrate critical data‡ have been used to complete these ANISN code checks. Results of the calculations are shown in table XVIII; the calculated  $k_{\text{eff}}$  should be equal to unity for a critical assembly. The agreement of calculations and experimental results is seen to be excellent and generally within 1%. The calculation procedure and cross-sections employed are thus judged to be quite acceptable for these cases. It should be recognized, however, that these assemblies are well moderated, whereas the volatility process models are not.

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\* Engle, W. W., Jr., A Users Manual for ANISN, A One-Dimensional Discrete Ordinates Transport Code with Anisotropic Scattering, Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, March 30, 1967 (K-1693).

† K-1717, loc cit, pp. 39, 41-43.

‡ The Hanford data were taken from the following reports: Physics Research Quarterly Report, July, August, September, 1962, Hanford Atomic Products Operation, October 15, 1962 (HW-75228), pp. 33-39; Physics Research Quarterly Report, October, November, December, 1962, Hanford Atomic Products Operation, January 15, 1963 (HW-76128), pp. 56-64; and Physics Research Quarterly Report, January, February, March, 1963, Hanford Atomic Products Operation, April 15, 1963 (HW-77311), pp. 40-47.

TABLE XVIII

## SUMMARY OF PLUTONIUM NITRATE CRITICAL CHECKS

Plutonium Concentration, g/l	Acid Molarity	Specific Gravity	Water, g/l	Total NO <sub>3</sub> , g/l	H/Pu	Critical Volume, liters	Calculated k <sub>eff</sub>
140*	2.2	1.307	882	284	171	12.97	0.994
44.5**	5.49	1.261	825	386	521	23.24	0.991
96*	1.67	1.219	719	203	258.3	12.99	0.996
53**	5.95	1.277	790	424	422.5	21.51	0.981
34**	2.06	1.124	930	163	740.6	22.52	0.991

\* Measured sphere volume was 12.95 liters, reflected with 0.049 inch stainless steel and water.

\*\* Measured sphere volume was 23.22 liters, reflected with 0.044 inch stainless steel and water.

#### Semiworks Interhalogen Plant Design

Designs have been prepared for modification of the semiworks plant for interhalogen (bromine pentafluoride) fluorination of the uranium oxides, regeneration of bromine pentafluoride, collection of products, and purification of the uranium. The designs of the regenerator and the distillation columns are discussed below. Preliminary drawings were made for all the necessary equipment, and separate piping diagrams were prepared for the reaction-regeneration-cold trapping portion of the plant and for the distillation system. In addition, instrument application drawings and a tentative layout were completed.

Regeneration Design. During the interhalogen fluorination of a fluidized mixture of U<sub>3</sub>O<sub>8</sub> and alumina in the semiworks system, the product gases from the fluid-bed reactor will first be fed to a regenerator for the conversion of the bromine back to the pentafluoride. The gas mixture will then be fed to a cold trap in which the uranium hexafluoride will be desublimed while the bromine pentafluoride condenses, allowing the bromine pentafluoride-rich phase to be drained from the cold trap. The solids in the trap will subsequently be distilled to remove entrained bromine pentafluoride. The decanted bromine pentafluoride phase, which will contain several percent uranium hexafluoride, may be vaporized and recycled to the fluid-bed reactor.

The reconversion of bromine to bromine pentafluoride is accomplished using elemental fluorine gas in a flame reactor type regenerator. Thermodynamically, several bromofluorides, including bromine monofluoride, bromine

trifluoride, and bromine pentafluoride can be produced when the bromine is reacted with fluorine. The halogen and interhalogen concentrations can be predicted from equilibrium data assuming that the kinetics for the various reactions are fast; in addition, the regenerator can be sized on the basis of the heat transfer requirements.

Computations based on the assumption of an adiabatic flame reaction indicate that the maximum flame temperature would be about 950°C. The equilibrium conversion of the bromine to the monofluoride, trifluoride, and pentafluoride as a function of temperature is depicted in figure 3. Figure 4 shows the heat removed (sensible heat plus reaction heat) when the gases are cooled from the flame temperature to the indicated outlet gas temperature.

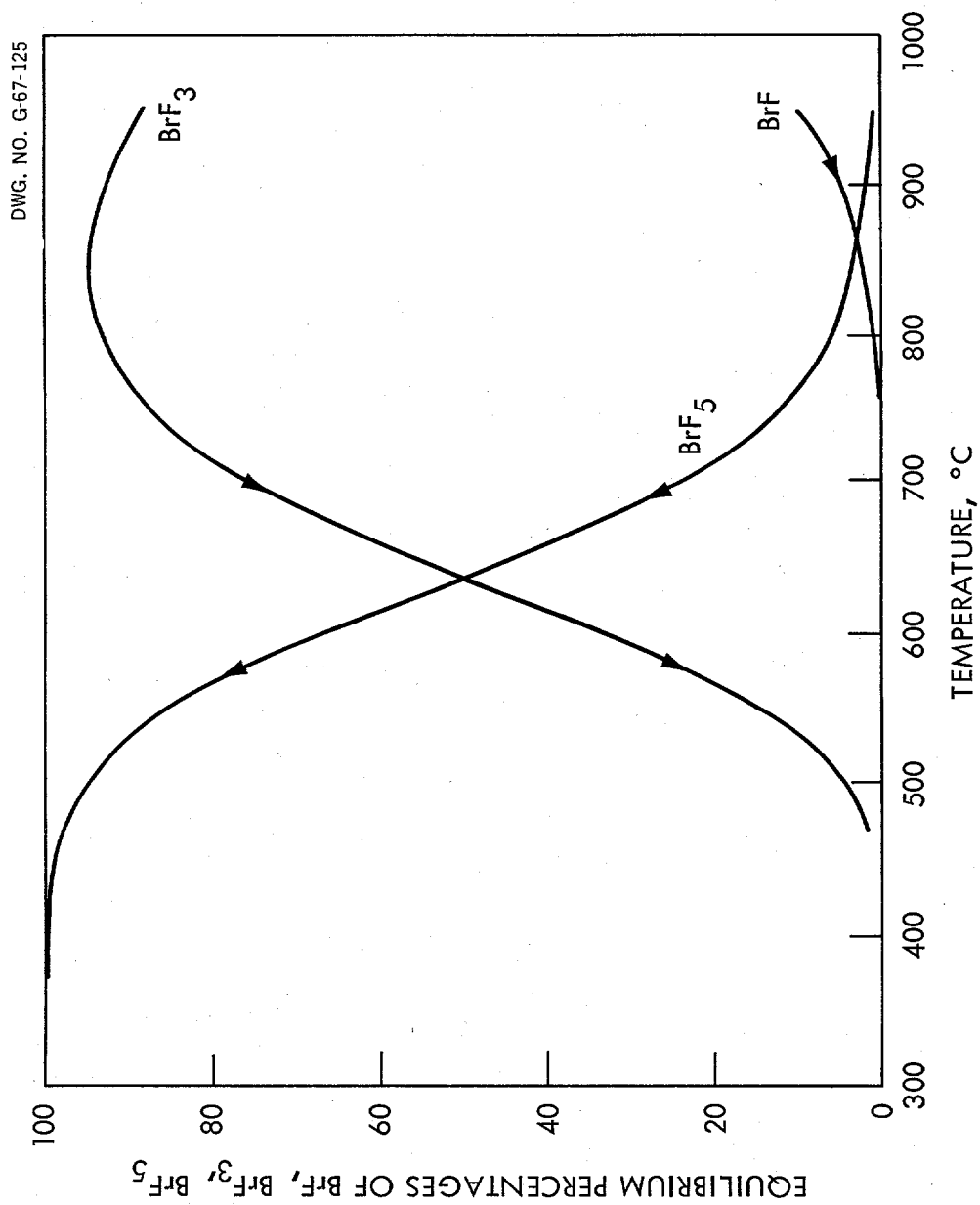
The total heat load for the regenerator has been computed to be about 44,000 Btu/hr based on essentially complete conversion to the pentafluoride. This heat will be removed by circulating air through several sets of cooling coils which will be attached to the outside wall. The maximum inside wall temperature will be held to about 260°C. The unit will be constructed of Monel, 6 inches in diameter, with a height of about 16 feet to ensure adequate cooling of the reaction gases even with no internal finning or packing. Some consideration is, however, being given to loading the bottom part with alumina balls to improve heat transfer and thus reduce the required height.

Uranium Hexafluoride-Bromine Pentafluoride Still for the Semiworks. In the semiworks operation, a distillation column will purify the uranium hexafluoride collected in the cold trap during the interhalogen fluorination. During one interhalogen cycle, about 190 pounds of uranium hexafluoride will be produced, and it is estimated that a maximum of 17 pounds (15 mole percent) of bromine pentafluoride will be retained in the uranium hexafluoride when it is charged to the still. The interhalogen fluorinations will be conducted on a batch basis during the tests; and accordingly, a batch still, 4 inches in inside diameter by 15 feet tall using 0.24-inch Cannon packing, has been selected for the application.

Data from ANL on the distillation of bromine pentafluoride-uranium hexafluoride mixtures indicate that the stage heights for a packed column are somewhat higher than for a standard n-heptane-methylcyclohexane system and that the relative amount of bromine trifluoride produced in corrosion reactions within the column becomes significant at bromine pentafluoride mole fractions below 0.001, causing an effective increase in stage height\*. High efficiency Cannon packing commonly exhibits a stage height of about 2 inches with the n-heptane-methylcyclohexane system, and on the basis of the above information, stage heights of 5 and 10 inches were assumed for the bromine pentafluoride-uranium hexafluoride system where the mole fraction of bromine pentafluoride was above and below 0.001, respectively. With these stage heights, it was calculated that the 15-foot column

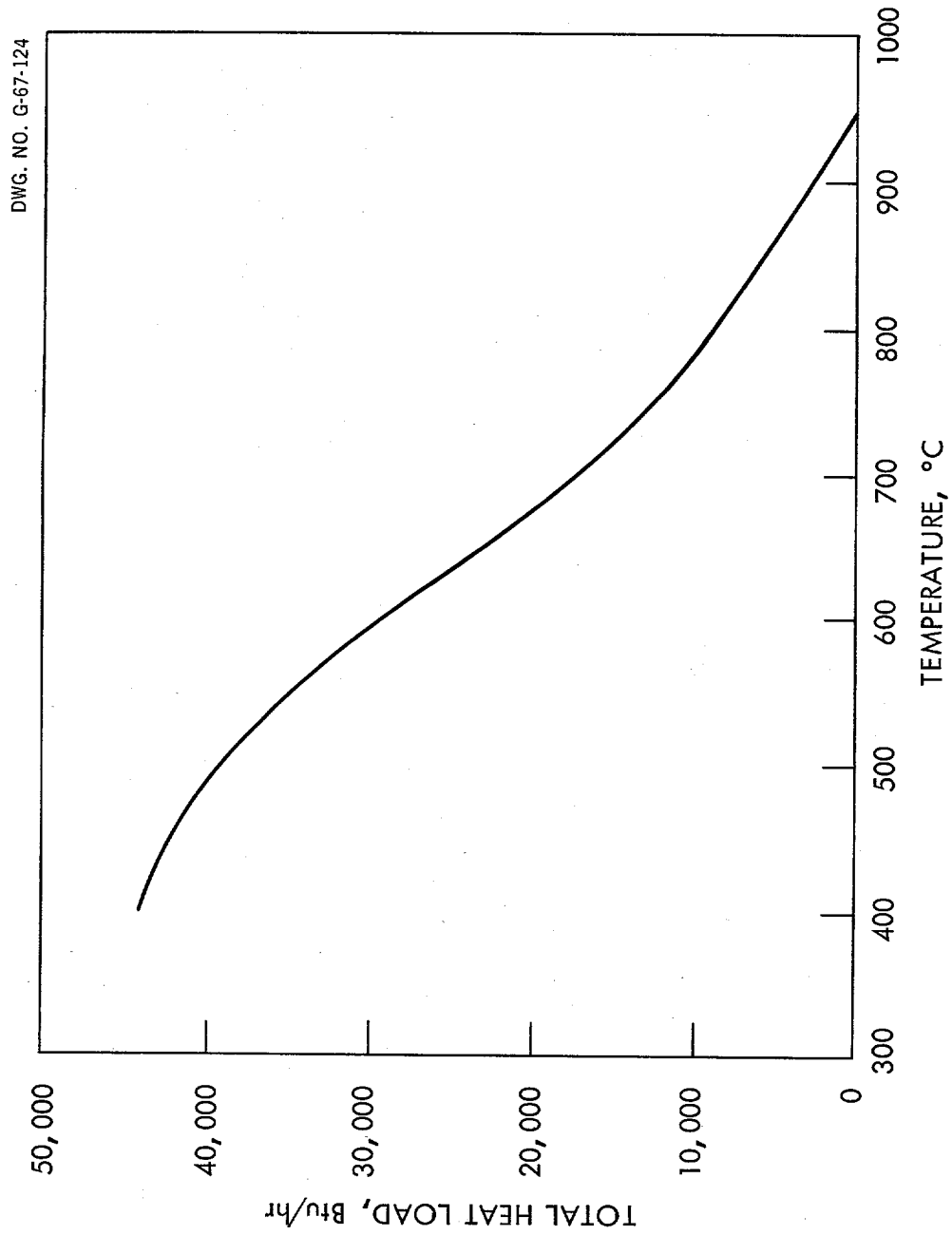
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\* Bromine pentafluoride-uranium hexafluoride distillation data appear in several ANL reports, including ANL-5668, -5896, -6003, and -6362.



EQUILIBRIUM CONVERSION AS A FUNCTION OF TEMPERATURE

Figure 3



REGENERATOR EXIT GAS EQUILIBRIUM HEAT LOAD  
ABOVE THE INDICATED TEMPERATURE

Figure 4

operated near total reflux would have a mole fraction of 0.75 bromine pentafluoride in the overhead product when the reboiler had reached a mole fraction of  $1.5 \times 10^{-5}$ , which corresponds to uranium hexafluoride of specification purity.

The flooding rate was calculated to be about 4,900 pounds per hour per square foot from a specialized correlation for Cannon packing\* and 9,600 pounds per hour per square foot from a generalized correlation for all packings\*\*. The conservative value of 4,900 pounds per hour per square foot was used in further calculations. A flow of 3,000 pounds per hour per square foot, or 60% of the flooding flow, was selected as the normal operating condition. In this range, the holdup in the 4-inch-diameter, 15-foot column was calculated to be about 35 pounds. Only about 2 pounds of this is bromine pentafluoride even during startup when the column is charged and then refluxed until it approaches steady state. Due to the comparatively low relative volatility, the reflux ratios required are fairly high being at least fifteen.

In order to calculate the length of time required for the distillation after the initial startup periods, the following assumptions were made:

1. The quantities of bromine pentafluoride and uranium hexafluoride in the column itself remain constant during the run, and only the reboiler contents are changed.
2. The reflux ratio is varied during the operation to obtain a constant composition overhead product.
3. The liquid flow rate in the column remains constant.
4. The reflux ratio at any time may be determined from the slope of the operating line intersecting the equilibrium curve at the composition in the reboiler.
5. In the range of interest (low bromine pentafluoride concentrations), the equilibrium line is straight.

Based on these assumptions, the time required for the mole fraction of bromine pentafluoride in the reboiler to drop to  $X_R$  was found to be

$$t = \frac{H_{Ro}}{L} \frac{(X_D - X_{Ro})}{(k - 1)} \left\{ \frac{1}{X_D} \left[ \ln \left( \frac{(X_D - X_R) X_{Ro}}{(X_D - X_{Ro}) X_R} \right) - \frac{X_R}{(X_D - X_R)} + \frac{X_{Ro}}{(X_D - X_{Ro})} \right] + \frac{k}{(X_D - X_R)} - \frac{k}{(X_D - X_{Ro})} \right\}$$

\* Pro-Pak Bulletin 23, Scientific Development Company, State College, Pa.

\*\* U. S. Stoneware Technical Data No. GR-109, Rev. 4.



where  $t$  = time,

$H_{Ro}$  = initial charge to the reboiler,

$L$  = liquid flow rate in the column,

$X_D$  = mole fraction bromine pentafluoride in the top product constant,

$X_{Ro}$  = initial mole fraction bromine pentafluoride in the reboiler,

$k$  = equilibrium mole ratio of bromine pentafluoride in the vapor phase to bromine pentafluoride in the liquid phase at low bromine pentafluoride concentrations, and

$X_R$  = mole fraction of bromine pentafluoride in the reboiler at time,  $t$ .

For the conditions expected in the semiworks, this equation predicts that specification uranium hexafluoride should be attained in the reboiler about 7 to 8 hours after draw-off is started. It is anticipated that several hours will be required after startup to establish steady-state conditions so that withdrawal of bromine pentafluoride can be initiated.

The column will most likely be operated until specification material is produced in the reboiler, and this material is accepted as product. The contents of the column itself, which will not be to specification, may be saved and added to the next charge. Using this procedure, the amount of uranium hexafluoride obtained as product will be about 80% of that charged to the still. In some cases, the distillation may be continued until the entire column contents reach specification, in which case, the recovery would be much higher for the single run. It should be pointed out, however, that on the basis of continued runs, recovery is as high with either scheme.

The problem of bromine trifluoride formation cannot be ignored, and one function of the semiworks column should be to determine the treatment necessary for bromine trifluoride removal. The column has been designed to operate as described if the bromine trifluoride can be held below specification levels by bubbling small quantities of fluorine through the column. If this is not sufficient, the reboiler product will have to be redistilled, taking the uranium hexafluoride product off the top and leaving the bromine trifluoride in the reboiler. Calculations indicate that the column should be of ample size to handle this question, although the total operation time would be approximately doubled due to the second distillation.

## PROTOTYPE TESTING AND EVALUATION

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Program work covered the zircaloy decladding, uranium dioxide oxidation, and fluorination phases of the volatility process. Projects included runs in the semiworks facility; elutriation and fluidization studies; filter testing; connector, sampler, and compressor evaluation; product purification tests; and two special runs in which discard alumina beds from ANL fluid-bed reaction studies with bromine pentafluoride were fluorinated with elemental fluorine. This last material was then sent to ORNL for use in their waste processing program.

### PROCESS AND REACTOR STUDIES

The semiworks fluid-bed oxidation tests initiated during the previous report period have been continued; chemical decladding and fluorination operations were included with several of the latest runs. Elemental fluorine was used as a stand-in for bromine pentafluoride, since facilities for handling the interhalogen had not been added to the plant.

Elutriation and fluidization tests were run in bench-scale equipment to explore elutriation rates for  $U_3O_8$  and alumina mixtures. Mixtures from reactor beds obtained from semiworks oxidation runs was employed. The work was conducted at ambient temperature in equipment constructed of transparent materials to permit easy viewing. Small-scale test data were sought which could be extrapolated for plant-scale applications.

### Semiworks Plant

Sixteen runs (UE-16 through -31) were conducted during this report period. For most of these tests, EGCR uranium dioxide pellets were charged to the reactor instead of the solid cylindrical uranium dioxide pellets used in the previously reported work through UE-15\*. Exceptions were in runs UE-22 and -23, where mixtures of alumina and  $U_3O_8$  powders were charged.

The EGCR pellets are annular cylinders made of ceramic uranium dioxide. The height and outside diameter are 3/4 inch; the inner hole diameter is 5/16 inch. Some breakage of pellets occurs during removal from the stainless steel clad fuel rods\*\*. Normally, more than 95% of the removed

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\* K-1717, loc cit.

\*\* The rods were removed from assemblies. The ends were cut off the rods. Each rod in turn was shaken using an electromagnetic vibrator to discharge the fuel. Fines generation was high until the pellet removal technique was perfected. The fines were charged in UE-20.

material is as essentially intact pellets, with the remainder graded down from relatively large pieces to fine dust. Only 1 to 2% is less than 20 mesh.

Over half of the runs were conducted with design capacity size (65 kg) uranium dioxide charges, with smaller charges for the remaining runs. Alcoa T-61 tabular alumina, nominally minus 48 plus 100 mesh, was used as the bed diluent in the reactor and as the cooling medium in the filter cooler. The charges for decladding tests were 0.17-inch-thick zirconium strip and/or 1/2-inch-diameter zircaloy-2 tubing. In each run, 1/2-inch T-164 Alcoa alumina balls were used to position the charges above the bottom of the reactor.

Decladding, oxidation, and fluorination tests were conducted individually or in various combinations. For the fluorination tests, UE-22, -23, and -29, elemental fluorine served as a stand-in for bromine pentafluoride. These tests were designed primarily as scoping studies, since hardware capability for use of bromine pentafluoride, the current flow sheet reagent for uranium fluorination, was not available. In the declad mode tests, UE-24 through -29, interest was focused on reliable operating conditions, reaction rate control, the degree of completion of the reaction, and the effects of the hydrogen chloride environment on both the system and subsequent process steps. Pellet oxidation was undertaken in all runs except UE-22 and -23, and each test was completed without major plugging of the bed. The minimum superficial velocities for the oxidation of shallow and deep pellet beds were evaluated, and several oxidation runs were made at conditions selected to increase the amount of  $U_3O_8$  fines elutriated from the bed.

Pertinent information on the run conditions, i.e., the charge weights, operation temperatures, reagent concentrations, etc., is contained in table XIX. Run results are summarized in table XX.

If elutriation of the  $U_3O_8$  from the alumina were successful, the process could be utilized in the two-vessel flow sheet in which the fines would be transferred from the declad-oxidation reactor to a fluorinator. In the semiworks plant, there is, of course, a single reactor; therefore, the fines are elutriated to the bottom of the filter cooler where they are mixed with the alumina cooling bed. Estimation of the amounts elutriated is therefore made after correction for the weight of the original alumina filter cooler charge.

Two simulated power reactor fuel assemblies were fabricated in ORGDP shops for use in future declad tests. The units were designed to fit in the 10-inch-diameter section of the reactor. Each assembly is 6 inches square and 4 feet long, and contains sixty zircaloy-2 tubes, 0.494 inch inside diameter by 0.033 inch wall thickness, in a square array on 3/4-inch centers. Two 3/8-inch-thick zircaloy end plates and a central 3/8-inch-thick zircaloy spacer plate are used to fix the positions of the tube. The assembly is held together by solid zircaloy rods, 3/8 inch in diameter, which run between the end plates. The tubes are loaded with 3/8-inch-diameter by 3/4-inch-long uranium dioxide pellets, and the weight of each





TABLE XX  
SUMMARY OF SEMIWORKS RUN RESULTS

	UE-16	UE-17	UE-18	UE-19	UE-20	UE-21	UE-22	UE-23	UE-24	UE-25	UE-26	UE-27	UE-28	UE-29	UE-30	UE-31
	Run Numbers															
Material Balances, (weight recovered X 100, weight charged)																
Gross Weight Basis	99.5	100.2	99.8	100.1	100.4			99.9	100.3	100.1	99.8	99.8	100.9	99.6	99.9	
Uranium Basis	102.0	100.6	99.8	101.4	99.9	96.2	103.0	100.6	99.0	102.0	98.4	98.6	99.0	99.7	101.5	
Decad Cycle																
Zirconium Remaining in Bed, Percentage of original zirconium charge*									3.1	+	4.7	2.4	1.9			
Oxidation Cycle																
Percentage of Pellet Charge:																
Oxidized to $U_3O_8$	97.2	99.2	99.7	96.6	95.2			59.5	98.2	95.8	98.7	94.6	97.6	99.1	97.6	
Comminuted to minus 35 meshs	100	100	99.7	95.9	95.1			56.8	99.8	99.8	99.8	96.4	+	94.9	95.4	
Percentage of Charge Elutriated from Reactor:																
Alumina Powder Plus Uranium Dioxide Pellets	7.5	9.9	10.9	27	9.4	8.0		25.5	32.6	57	54.2	58.1	55.7	29.3	10.8	
Uranium	0	26.7	25.7	32	16.9	12.4		29.6	55.2	79.0	93.7	91.3	91.0	53.0	20.9	
Alumina Powder	7.5	0.2	1.7	24.7	1.8	3.8		19.7	4.4	40.9	15.8	8.7	3.5	0	0	
$U_3O_8$ Equivalent in Elutriated Material, %	-	99	88.6	38.8	91.4	75.8		63	93.6	71.1	87.0	93.9	97.5	100	100	
Fluorination Cycle																
Uranium Concentration in Bed at End of Test, %							0.42	1.25						0.15		
Percentage of Uranium Charge Elutriated to Filter Cooler							17.3	42.2						39.1		
Percentage of Charge Recovered as Uranium Hexafluoride							78.3	57.7						59.5		

\* The chlorine concentration of the bed was not determined; therefore, the amount of unreacted zirconium metal remaining in the bed cannot be estimated.

+ Not determined.

§ The numbers recorded represent the situation after light pressure was applied to break up soft agglomerates.

element is about 76 kg with 53 kg being uranium dioxide pellets. The fabrication details are shown in figure 5, and a completed unit is shown in figure 6.

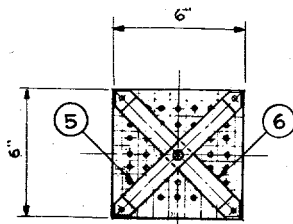
Run commentaries are as follows:

#### Runs UE-16 and UE-17

During oxidation runs UE-12 through -15, the material elutriated from the reactor to the filter cooler averaged 92%  $U_3O_8$ , but the actual amount of uranium transferred represented only a small portion (10 to 25%) of the total uranium charge. The superficial velocity ranged from 0.6 to 0.75 ft/sec in the 10-inch-diameter section of the reactor.

Runs UE-16 and -17 were undertaken to evaluate the effect of a velocity of 1.25 ft/sec in the 10-inch-diameter section on elutriation. Run UE-16 was undertaken to establish the magnitude of alumina elutriation at the new velocity using oxidation run size charges and conditions but with nitrogen only instead of an oxygen-nitrogen mixture. The alumina powder and the upper half of the pellet bed were heated to 482°C, while the bottom half of the pellet bed and the lower section of the reactor were 316°C. The gas flows were adjusted to give actual velocities of 3.0 and 1.25 ft/sec in the reactor 5- and 10-inch-diameter sections, respectively. The temperature of the lower pellet bed was subsequently raised to 482°C to simulate operating conditions at the end of the oxidation. The test ran for 6 hours, and at the conclusion, 4.6 kg of alumina had been transferred to the filter cooler.

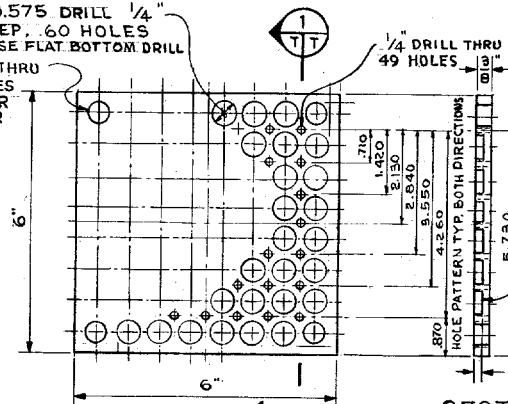
After the run, the elutriated alumina was returned to the reactor for run UE-17, so that the charge for this new run was the same as for UE-16. In addition, the same operating conditions were employed, except that after heatup to reaction temperature with nitrogen as the fluidizing medium, the nitrogen was replaced with air. The oxidation reaction was initiated at the top of the pellet bed by keeping the upper portion at 482°C and all points below the top 6 to 8 inches of pellets at 316°C. As the oxidation of the original upper portion was completed, progressively lower portions of the pellet bed were raised to 482°C. Later, to finish the run, the temperature of the entire bed was raised to 565°C. There were no indications of plugging, channeling, or temperature excursions during the run. Reaction time for the test was 5 hours. Elutriation selectivity for uranium was good; 8.2 kg of uranium (26.7% of the uranium charge) and less than 0.1 kg of alumina (0.15% of the alumina charge) were elutriated to the filter cooler. This composition is equivalent to 99%  $U_3O_8$ . The final reactor bed contained some soft powder balls ranging from 1/16 to 1/4 inch in diameter, equal in weight to 3.9% of the original pellet charge. When this material was placed on a 35-mesh screen and light pressure was applied, disintegration took place. The powdered fines, which were thus produced, passed through the screen, leaving a mere 21 grams of plus 35 mesh. Consequently, the oversize would probably fluorinate readily enough.



PLAN

SCALE: 1/4" = 1"

0.575 DRILL 1/4" DEEP, 60 HOLES USE FLAT BOTTOM DRILL  
1/2" DRILL THRU 4 HOLES ONE PER CORNER



PART 1

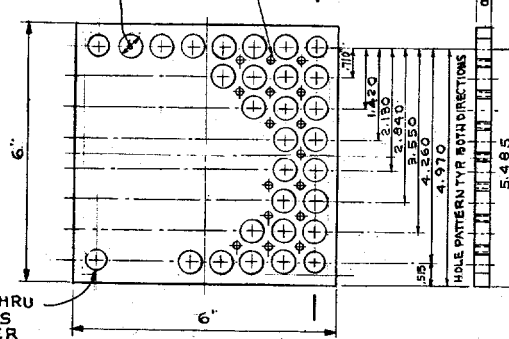
SCALE: 1/2" = 1"

SECT 1/T

NOTE

SPACING OF .575 AND 500 HOLES TO BE THE SAME FOR PARTS 1 & 2

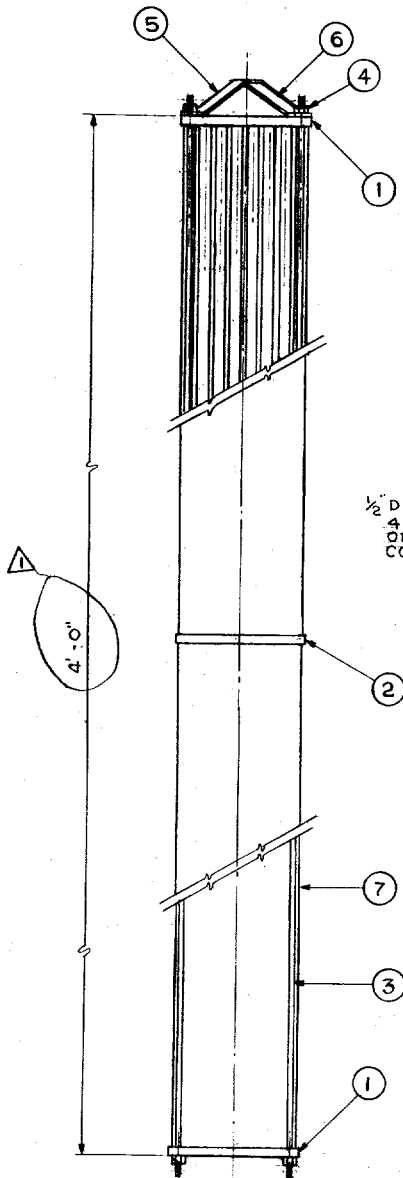
.575 DRILL THRU 60 HOLES  
1/4" DRILL THRU 49 HOLES



PART 2

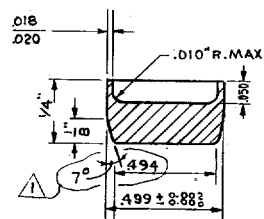
SCALE: 1/2" = 1"

SECT. 2/T



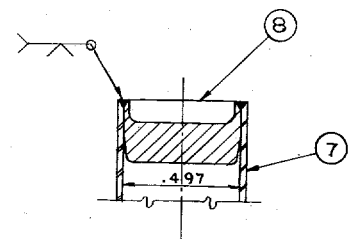
ELEV. ASSEMBLY

SCALE: 1/4" = 1"



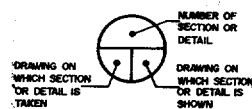
PART 8

NO SCALE



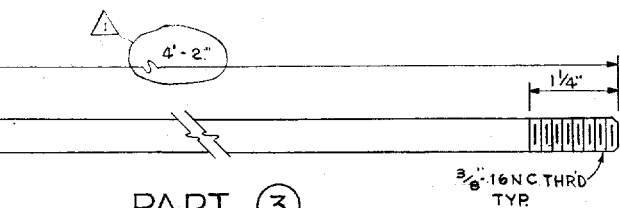
DETAIL TUBE END CLOSURE

NO SCALE

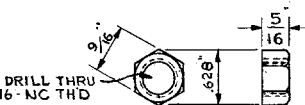


SECTION & DETAIL KEY

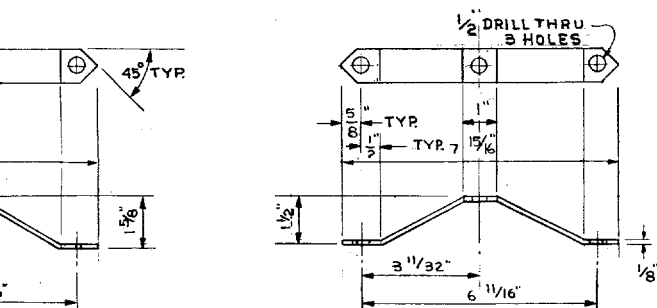




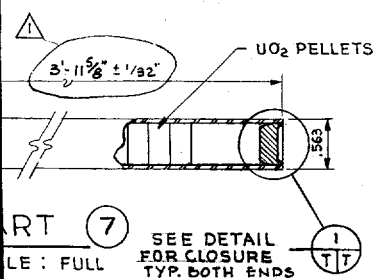
**PART 3**  
SCALE: FULL



**PART 4**  
SCALE: FULL



**PART 6**  
SCALE: 3/8" = 1"



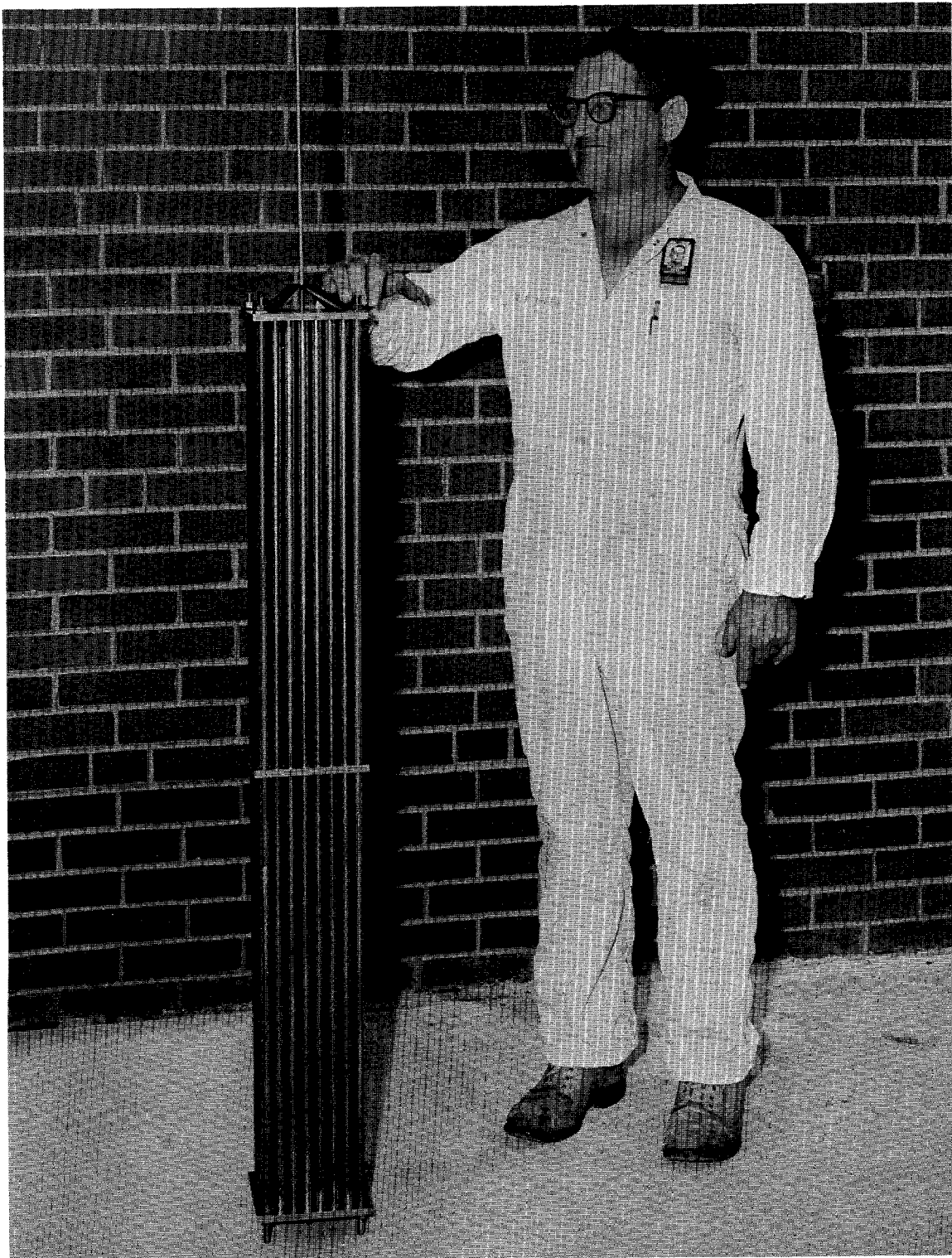
**PART 7**  
SCALE: FULL

# **PARTS LIST**

PART NO.	QTY. NO.	NO. REQD.	DESCRIPTION (NAME, SIZE, ETC.)	MATERIAL
1	D-P33750T	2	PLATE 3/8 THK X 6" X 6" SQUARE	ZIRCALOY-2
2	"	1	PLATE 3/8 THK X 6" X 6" SQUARE	ZIRCALOY-2
3	"	4	ROD 3/8 DIA. X 4'-2" LONG	ZIRCALOY-2
4	"	1	3/16 HEX. BAR STOCK 4" LONG	ZIRCALOY-2
5	"	1	BAR 1/8 THK X 1" WIDE X 11" LONG	ZIRCALOY-2
6	"	1	BAR 1/8 THK X 1" WIDE X 11" LONG	ZIRCALOY-2
7	"	60	TUBE 0.563 X 0.033 WALL THK X 3'-11 5/8" LONG	ZIRCALOY-2
8	"	1	ROD 5/8 φ X 3'-3" LONG	ZIRCALOY-2

**SIMULATED FUEL  
ELEMENT DESIGN**

**Figure 5**



COMPLETED SEMIWORKS FUEL ELEMENT

Figure 6

Run UE-18

In previous runs, it was established that a superficial gas velocity of 3 ft/sec was sufficient to keep a pellet bed purged of powder during an oxidation run in which the reaction was forced to occur at the top of the pellet bed which was on the order of 1.4 feet deep initially. Run UE-18 was undertaken to determine if as low a velocity as 2 ft/sec was satisfactory. With the exception of this lower superficial velocity in the 5-inch-diameter section, the operating conditions for UE-18 were the same as UE-17.

The reaction zone was held at the top of the pellet bed by maintaining the temperature of the upper 6 to 8 inches at 482°C while holding temperatures below this zone at 316°C. Eventually, the entire bed was heated to 482°C and then to 565°C to ensure completion of the oxidation. No plugging, channeling, or temperature excursions were noted, but at the end of the run, there were plus 35-mesh powder balls in the product from the reactor. The weight of this material was equal to 5.2% of the pellet charge, but after gentle rubbing on a 35-mesh screen, only 29 grams of hard oversize material was left.

After oxidation was complete (5 hours' reaction time), the material elutriated was removed from the filter cooler and receiver. The run was then continued for another 5 hours at the same operating conditions. Analysis of the results indicated that, during the initial 5 hours of oxidation, 3.9% of the reactor alumina-plus-pellet charge was elutriated; the mixture contained 8.1% of the uranium charge and 1.3% of the alumina charge. During the second 5-hour period, an additional 7% of the original reactor alumina-plus-pellet charge was elutriated; this material consisted of 17.6% of the uranium charge and 0.4% of the alumina charge.

Run UE-19

The purpose of UE-19 was to test oxidation in a deeper pellet bed than used heretofore. The charge for this run was increased to 65 kg of uranium dioxide pellets, thus resulting in a bed depth in the 5-inch-diameter section of 3 feet 4 inches, or about twice as deep as in previous successful oxidation runs. As for the past 3 runs, the alumina powder-to-uranium charge ratio was kept at 2.0. Oxidation was again promoted at the top of the pellet bed by keeping the upper 6 to 8 inches at 482°C and the lower pellets at 316°C. Air was used as the oxidant.

The gas velocity was initially set at 2 ft/sec in the 5-inch-diameter section of the reactor as in run UE-18; however, after about 25% of the charge had been reacted, the bed pressure drop had increased from an initial 4 psi to about 16 psi. Because of the possibility of bed plugging, the velocity was then increased to 3 ft/sec, and after about an hour, the bed pressure drop had decreased to 7 psi where it remained for the rest of the run. The run lasted 10-1/4 hours.

During UE-19, 99.7% of the pellet charge was oxidized. In a sieve analysis of the contents of the reactor after the run, 10.1% of the weight of the

pellet charge was found to be plus 35-mesh material. After rubbing on a 35-mesh screen, the amount of plus 35-mesh material was reduced to 0.3 weight percent of the charge.

The filters were removed from the filter cooler for examination. A thin powder coating (estimated to be 1/64 inch thick) was found over about 80% of the filter area; the remaining 20% was essentially bare. These filters had not been examined but had performed satisfactorily since UE-7. This period covers an oxidation period of 77.5 hours and a total run time of 100 to 125 hours.

#### Run UE-20

The most successful oxidation runs to this point were made with an alumina-to-uranium charge ratio of 2.0. This ratio would, in all likelihood, be lower in actual plant operation, since alumina requirements and the generation of solid waste would thus be minimized. UE-20 was conducted to study the effect of a 1.2 charge ratio. The gas velocities were 2.5 and 1.5 ft/sec, respectively, in the 5- and 10-inch-diameter sections. The pellets were charged to the 5-inch-diameter section, and the resultant uranium dioxide bed was 1 foot 8 inches deep.

Oxidation was limited to the top of the pellet bed by the temperature control method used in previous runs. There were no temperature excursions, and the maximum bed pressure differential was about 11 psi. The oxidation was conducted satisfactorily using air, with 96.6% of the pellet charge reacted and 95.9% comminuted to minus 35-mesh powder. The run lasted 5-3/4 hours. A pressure of greater than 45 psig was required to initiate fluidization, which is 5 to 10 psi more than normally is required. This high starting pressure requirement probably resulted from the unusually high concentration of uranium dioxide fines in the charge. The fines were all generated during the "learning" phase of the pellet removal operation. Previous pellet charges have been almost entirely plus 3 mesh. In a screen analysis of this charge, only 39% was plus 3 mesh, while 41% was minus 3 plus 12 mesh, and 20% was minus 12 mesh. Fluidization during the run was good, as indicated by the normal reactor inlet pressure and pressure drop oscillations.

#### Run UE-21

This run was performed with a shallow pellet bed which was located entirely in the 10-inch-diameter section of the reactor. The pellet charge amounted to 56.5 kg, and the bed depth was 9 inches. The reactor was filled with 1/2-inch alumina balls to a level approximately 6 inches above the top of the 5- to 10-inch-diameter transition section to support the pellets. The temperature of the reactor bed from the pellet bed down was held at 316°C, and that of the fluidized alumina above the pellets at 482°C. Enough heat was transferred from the alumina to the pellets to cause reaction at the top of the bed. Air was used as the oxidant. After 80% of the charge had been reacted, the bed temperature was gradually increased to 565°C to complete the oxidation. At the end of the run, 95.2% of the pellet charge had been oxidized, and 95.1% had been converted to minus 35 mesh. The

operating time was 9-3/4 hours. There had been no indications of plugging, channeling, or temperature excursions.

#### Runs UE-22 and -23

These runs were made to check out the semiworks system in a fluorination environment using elemental fluorine.

The charge for UE-22 was the reactor bed from UE-21 after oxidation. This bed contained 45.1%  $U_3O_8$  and 54.9% alumina. Sufficient 1/2-inch-diameter alumina balls were used to position the bottom of this powder approximately 1 foot 10 inches above the bottom flange of the reactor. As a result, the top of this bed, when not fluidized, was about 2 feet above the top of the 5- to 10-inch-diameter transition section. The bed was fluidized with nitrogen and heated to 316°C; then sufficient fluorine was admitted to give an inlet gas concentration of 15% fluorine in nitrogen. The operating superficial velocities were 0.75 ft/sec in the 5-inch-diameter section and 0.2 ft/sec in the 10-inch-diameter section. The gas velocity in the filter cooler was 0.1 ft/sec. Little reaction was noted at these conditions, so the fluorine concentration was increased to 30%. Since there was still little evidence of reaction; the bed temperature was increased to 371°C, at which temperature the reaction rate was sufficient to necessitate the use of cooling air through the coils on the wall of the reactor. The gas flow was continued for 5-1/2 hours; however, there was no further indication of reaction after 5 hours. The uranium hexafluoride product was collected in four minus 73°C cold traps in series. During the reaction, 9.0 kg of material, consisting of 17.3% of the uranium charge and 1% of the alumina charge, was elutriated from the reactor. The reactor temperature was easily controlled, and the bed material in the reactor at the end of the test contained 0.42% uranium.

The charge for run UE-23 was the final reactor bed from UE-17, which contained 32.4%  $U_3O_8$  and 67.6% alumina. The bed position was approximately the same as for UE-22. The bed was fluidized with nitrogen and was heated to 316°C; then, flows were adjusted to give 30% fluorine and superficial gas velocities of 0.75 ft/sec in the reactor 5-inch-diameter section and 0.2 ft/sec in the 10-inch-diameter section. As soon as the fluorine flow was initiated, a hot spot developed in the lower portion of the bed, and the internal temperature exceeded 649°C. The fluorine flow was immediately stopped, and the bed temperatures were again stabilized at 316°C. At this point, the reactor heaters in the 5-inch-diameter section were turned off, and cooling air was applied to the reactor wall until the wall temperature began to decrease. The gas flows were then resumed at the previous levels, and the temperature was easily maintained between 371 to 400°C. Fluorine was admitted for 4-3/4 hours. During the run, 16.8 kg of material was elutriated from the reactor; this consisted of 42.2% of the uranium charge and 1.8% of the alumina charge. The uranium concentration in the bed at the end of the test was 1.25%.

The residual uranium contents of the beds after both UE-22 and -23 were higher than expected. Of course, it is not intended in these runs to maximize the percentage fluorination. In all probability, the residual

uranium content would have been lower with different operating conditions, such as a longer fluorination period and use of higher fluorine concentrations at the end of a run. The amount of  $U_3O_8$  elutriated is sufficiently large that, for successful plant operation, provision must be made for the return of the oxide to the fluorinator.

#### Run UE-24

Run UE-24 was made to check the semiworks system operation under hydrogen chloride gas feed conditions without zircaloy being present; a hydrogen chloride exposure step was followed by an oxidation cycle. In addition, a superheated steam system was installed which permitted 50 psig,  $316^\circ\text{C}$  steam to be injected into the filter cooler off-gas line 2 inches before its entrance into the scrubber. This system was provided so that zirconium tetrachloride and stannous chloride might be hydrolyzed before entering the scrubber in the dechlor runs. Additionally, three of the six filter tubes in use since UE-7 were removed, so UE-24 was conducted with only three filter tubes.

The 1/2-inch alumina balls were used to position the bottom of the pellet bed approximately 1 foot above the top of the 5- to 10-inch-diameter transition section. The pellet bed depth was 9 inches, and the depth of the alumina bed at rest was 2 feet. The distance from the top of the alumina bed to the reactor off-gas outlet line was then approximately 6 feet 6 inches.

The bed was fluidized with nitrogen and was heated to  $400^\circ\text{C}$ . The filter cooler was held at approximately  $316^\circ\text{C}$ , and the gas lines were maintained at  $316$  to  $343^\circ\text{C}$ . With these temperatures stabilized, the gas flows were adjusted to give a concentration of 20% hydrogen chloride and 80% nitrogen, and a velocity of 0.5 ft/sec in the 10-inch-diameter section calculated at operating temperature and pressure,  $400^\circ\text{C}$  and 2 psig. These conditions were maintained for 1 hour, and then the gas composition was changed to 40% hydrogen chloride and 60% nitrogen with the gas velocity and temperatures held constant. After another hour, the concentrations were set at 60% hydrogen chloride and 40% nitrogen.

After a total of 3 hours, the hydrogen chloride flow was discontinued, the system was purged with nitrogen, and the system conditions were adjusted for oxidation. About 3 hours was required to stabilize at oxidation conditions which were reactor bed temperatures, including the pellet bed,  $316^\circ\text{C}$ ; and the filter cooler and gas lines,  $121^\circ\text{C}$ . The superheated steam flow was stopped. In an attempt to promote elutriation of  $U_3O_8$  from the reactor as it was formed, the superficial gas velocity in the 10-inch-diameter section was raised to 2.5 ft/sec (calculated at  $482^\circ\text{C}$  and 2 psig), and the oxidation rate was limited by holding the inlet oxygen concentration at 1%. After the first 1-1/2 hours of oxidation, the pressure drop across the filter tubes increased from an initial value of 1-1/2 to 3 psi; the pressure drop remained at this level for the duration of the run. The reaction rate at 1% oxygen was slow; and during the last 4-1/2 hours of operation, 3% oxygen was used. Malfunction of the oxygen analyzer created an uncertainty as to the degree of oxidation.

During the run, 31.6 kg of material was elutriated. Elutriation selectivity for uranium was not good; the elutriated material contained only 63.2%  $U_3O_8$ . In addition, only 57% of the pellet charge was converted to minus 35-mesh powder, probably because of the low oxygen concentrations used and the malfunction of the oxygen analyzer.

#### Run UE-25

UE-25 was the first semiworks run in which zircaloy was reacted with hydrogen chloride. The charge for this run was the same as for UE-24, except that 6.5 kg of zircaloy was also added and the uranium charge consisted of 27.9 kg of plus 35-mesh material from UE-24 (essentially all uranium dioxide) and 37.1 kg of fresh pellets. No additional filters were installed; therefore, UE-25 was conducted with the same three filters used in UE-24. The uranium dioxide bed depth was 10 inches, and the alumina bed depth was 2 feet 5 inches. The zircaloy charge consisted of eleven tubes, 8 feet long by 0.454 inch inside diameter with a 0.033 inch wall thickness. Ten of the tubes were 4 feet long, while the other was 8 feet long; thus before fluidization, the shorter tubes extended above the bed 1 foot 7 inches and the long tube 5 feet 7 inches.

Conditions prior to starting hydrogen chloride feed were the same as for the hydrogen chloride trial cycle in UE-24. Initial hydrogen chloride feed was at a concentration of 20% hydrogen chloride, 10% hydrogen, and 70% nitrogen. The hydrogen was added to simulate conditions expected in a plant employing hydrogen chloride recycle. Approximately 15 minutes after the hydrogen chloride flow was started, the scrubber water discharge stream became cloudy.

Over the next 2-1/2 hours, the concentrations of hydrogen chloride and hydrogen in the inlet gas were increased stepwise to 60% hydrogen chloride and 30% hydrogen. The scrubber water became increasingly opaque (apparently because of increasing concentrations of zirconium dioxide), the internal temperatures in the sections above the fluid bed zone rose as much as 40°C, and the pressure downstream of the filter cooler increased about 3 psi, indicating a tendency for the filter cooler off-gas line to plug. The inlet gas composition was adjusted to 40% hydrogen chloride and 30% hydrogen, and the plugging tendency was overcome by rapping the flange at the gas entrance to the scrubber. Three hours later, when the zircaloy-hydrogen chloride reaction appeared to taper off, the hydrogen chloride concentration was raised back to 60% to complete the operation.

The hydrogen chloride cycle was followed by oxidation of the uranium dioxide at 482°C. An attempt was made to operate at a gas velocity of 2.5 ft/sec in the 10-inch-diameter section, but the filter pressure drop exceeded 10 psi. The operation was, therefore, conducted at a velocity in the 10-inch-diameter section of 1.05 ft/sec at operating conditions (482°C and 9.2 psig). The oxygen concentrations used were in succession 5%, 10-1/2%, and 21% in nitrogen for 1, 2, and 5 hours, respectively. Under these conditions, the pressure drop across the filters was about 6 psi. The zonal temperature control technique, to limit the oxidation

reaction to the top of the pellet bed, was not employed because it was judged unnecessary for the shallow bed.

The total run consisted of a 7-1/2-hour hydrogen chloride cycle (hydrogen chloride flow time) and an 8-hour oxidation cycle. The charge had been reduced to approximately 0.2 kg of plus 35-mesh material and 32.6% of the reactor alumina-plus-pellet charge (55.2% of the pellet uranium charge) had been elutriated. Chemical analysis indicated that 98.2% of the pellet charge had been oxidized.

Prior to the hydrogen chloride cycle for this run, the system had been flow tested with nitrogen at 17, 20, 27, and 33 scfm, with the filter cooler at 316°C. These in-place tests were repeated after the system had been emptied following the oxidation cycle, and it was found that the throughput flow rate per square foot of filter surface per pound per square inch pressure drop across the filter tube was 17 to 25% of that before the run, based on the assumption that the total tube area, i.e., 8.1 square feet, was available for flow.

The three filters used in this run (numbers 4, 5, and 6), were then removed from the system, checked in a filter flow test station, water washed, dried, and again checked. The results are given in table XXI and are compared with flow data taken at the station on the three tubes which had been through all runs through UE-23 but then removed (numbers 1, 2, and 3). The permeability of each of the three filter tubes, which were cleaned and washed after UE-25, was about equal to that of a new tube and slightly greater than the permeability of the three filters that had been used through UE-23\*.

#### Runs UE-26 and -27

These runs were made to study the dechlorination and oxidation reactions when the main reactor was loaded with uranium dioxide pellets and a bound bundle of alumina-filled zircaloy tubes. This charge was considered a first step approach in the simulation of a process plant charge for semiworks tests.

Prior to UE-26, the following system changes were made:

1. All six of the filter tubes for which flow data are given in table XXI were placed in service, making the filtering area 16.2 square feet.

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\* In-place cubic foot per minute per square foot per psi flow rate data are obtained under operating conditions when filters are mounted in the hot filter cooler. These data are naturally not expected to agree with flow rate measurements taken on the same filters one at a time in laboratory type flow test equipment at room temperature. In-place tests are run to follow plugging tendencies in operating equipment; the data obtained are undoubtedly influenced by the operating conditions and the arrangement of the filters within the housing shell.



TABLE XXI

SUMMARY OF DATA IN FILTER FLOW TEST STATION  
(Run UE-25)

Tube	Before Washing			After Washing		
	Pressure Drop, psi	Flow, scfm	Flow Rate, scfm/sq ft-psi	Pressure Drop, psi	Flow, scfm	Flow Rate*, scfm/sq ft-psi
1†	0.05	13.7	103	-	-	-
2†	0.06	13.7	84	-	-	-
3†	0.08	13.7	63	-	-	-
4†§	1.76	11.2	24	0.04	13.7	127
5†§	1.54	11.2	27	0.03	13.7	169
6†	1.29	11.2	32	0.03	13.7	169

\* A new filter tube should have a pressure drop of approximately 0.035 psi at 14 scfm and a flow rate of about 150 scfm/sq ft-psi. Variations in this flow rate have been found.

† Filter tubes 4, 5, and 6 were used in the decladding run UE-25, while tubes 1, 2, and 3 were not. Both sets were employed in all oxidation runs through UE-23.

§ With the test apparatus, the flow rate of 13.7 scfm could not be obtained on tubes 4 and 5 due to the extent of plugging before washing.

2. The superheated steam injection nozzle was moved from its position, about 2 inches from the scrubber inlet, to a point approximately 6 feet from the scrubber inlet in an attempt to provide longer retention time for hydrolysis of the zirconium tetrachloride and thus eliminate the plugging difficulties which apparently occurred at the entrance to the scrubber in run UE-25.

The zircaloy charges for runs UE-26 and -27 consisted of 12 tubes, 8 feet long. One end of each tube was pinched shut, and the tubes were bound together with zircaloy wire and were then filled with part of the 59 kg alumina charge. The zircaloy charge for UE-26 was 7.2 kg, and for UE-27, the charge was 7.4 kg. The remainder of the charge was the same as that for runs UE-24 and -25. Operating conditions for the hydrogen chloride and oxidation cycles were similar to those of UE-25. During

both the de-clad and the oxidation cycles, the reagent gases were added in increasing concentrations as the reactions progressed. Just as in UE-25, no attempt was made to oxidize the pellet bed from the top. Oxidation was 95.8% complete in UE-26 and 98.7% complete in UE-27. Small amounts of plus 35-mesh material were found in the reactor bed after completion of oxidation (0.2 kg for UE-26 and 0.1 kg for UE-27). During oxidation, large amounts of  $U_3O_8$  were elutriated (79.0 and 93.7% of the uranium reactor charges for UE-26 and -27, respectively). In contrast,  $U_3O_8$  elutriation in previous semiworks tests has been considerably less (see table XX). The pressures in the reactor during oxidation were 4.2 psig for the first run and 10.8 psig for the second, the higher pressure being attributed to decreasing filter permeability.

In-place flow tests were conducted before and after both UE-26 and -27 with 17 and 33 scfm of nitrogen, respectively, passing through the filters. The temperature of the filter cooler was kept at 316°C. Increases in pressure drop over the course of the runs amounted to less than 1 psi at both flows.

#### Run UE-28

In the first semiworks de-clad runs with zircaloy, i.e., UE-25 through -27, the charges of the alloy ranged from 6.8 to 7.4 kg. The test zircaloy-clad fuel element assemblies, which were fabricated at ORGDP, contain about 23 kg of zircaloy. Accordingly, to investigate the effect of a large quantity of metal, such as is included in the test assemblies, the charge for UE-28 included 16 kg of 0.170-inch-thick zirconium strip and twelve zircaloy tubes weighing 6.8 kg. The zircaloy tubes were 0.454 inch inside diameter by 0.033 inch thick by 8 feet long and were bound tightly with zircaloy wire. The lower end of each tube was crimped closed, and eleven of the tubes were filled with minus 48- plus 100-mesh alumina. One of the center tubes in the cluster was fitted with a 1/4-inch-diameter nickel tubing thermowell. Four thermocouples were inserted for temperature measurements at 0-, 2-, 4-, and 6-foot levels from the lower end of the tube.

Alumina balls were used to position the bottom of the uranium dioxide pellet bed approximately 1 foot above the top of the 5- to 10-inch-diameter transition section of the reactor. The zircaloy and zirconium charges were placed on top of the alumina balls, the 65 kg of EGCR type uranium dioxide pellets was then added, and the alumina powder was added last. The pellet bed depth was 10 inches; the lower 10 inches of the zircaloy and zirconium were embedded in the uranium dioxide pellet bed. A total of 45.5 kg of alumina powder was used to fill the tubes and to provide a 1-foot 10-inch alumina bed. Approximately 5 feet 4 inches of the zircaloy tubing and approximately 2 feet 2 inches of the zirconium strip extended above the bed when settled. The six filters used in UE-26 and -27 were reused for this run without intermediate cleaning.

The reactor bed temperatures for de-cladding were 400 to 415°C, and gas preheater outlet temperatures ranged from 315 to 330°C, and the filter cooler temperatures were 290 to 325°C. The superficial gas velocity in

the 10-inch-diameter section of the reactor was 0.5 ft/sec at 400°C and 2 psig. Thermocouples in the tube read a maximum of 11 to 14°C higher than those in the bed throughout the reaction period. The cycle consisted of 4 hours at 20% hydrogen chloride, 10% hydrogen, and 70% nitrogen; 4 hours at 40% hydrogen chloride, 30% hydrogen, and 30% nitrogen; and 7 hours at 60% hydrogen chloride, 30% hydrogen, and 10% nitrogen. After the hydrogen chloride cycle, the filter cooler and receiver were emptied, and 11.7 kg of fresh alumina was charged to the filter cooler.

The oxidation cycle consisted of 3 hours at 10.5% oxygen and 4 hours at 21% oxygen. The reactor bed temperature was 480°C, the filter cooler temperature was 315°C, and the operating pressure in the reactor was 9.5 psig. After the run, 2.4 kg of the charge remained as plus 35-mesh material. Pellet comminution was thus about 96.4%; however, analysis indicated only 94.6% completion of the oxidation reaction. Approximately 58.1% of the pellet uranium-plus-alumina charge was elutriated, including about 91.3% of the uranium but only 8.7% of the alumina charge.

Upon removal of the reactor bed following the run, it was found that essentially all of the zircaloy and zirconium had been consumed, since there was no visible evidence of the metals.

In-place tests conducted before and after the run with the filter cooler at 315°C using 17 and 33 scfm of nitrogen showed increases in filter pressure drop from 1.0 to 9.6 psi at the lower flow, and from 1.7 to 11.8 psi at the higher flow. As mentioned previously, none of these filters had been cleaned since UE-25. Decreases in the flow rate measured in terms of cubic feet per minute per square foot of filter surface per pound per square inch pressure drop across the filter tube over the course of runs UE-26 through -28 were computed to be 98% at 17 scfm and 93% at 33 scfm. After the in-place tests, the filter tubes were vacuumed and brushed, and then water washed.

The filters were tested in the flow test station. The average gas flow rate after vacuuming for tests run at room temperature and pressure was 10.7 cfm/sq ft-psi and after water washing, it was 59.8 cfm/sq ft-psi. This latter figure is equivalent to about 35 to 40% of the flow rate of an unused tube and approximately 75% of the flow rate of the tubes after use in oxidation runs UE-1 through -23, which, of course, had not been exposed to hydrogen chloride.

#### Run UE-29

The charge for run UE-29 was similar to that for UE-28 except that the zircaloy tubes were held together in a 3 by 4 rectangular array by 0.170-inch-thick zirconium plates drilled to provide 3/4-inch center-to-center spacing for the tubes. The form in which the zircaloy was present consequently resembled the geometry of a fuel element more closely than any declad charge up to this point. A complete processing cycle was undertaken; decladding, oxidation, and fluorination.

Temperatures and superficial velocities for the de-clad and oxidation were the same as for UE-28. Both the de-clad and oxidation cycles were run using stepwise increases of reagent gas in nitrogen. After both the hydrogen chloride and the oxidation cycles, the filter cooler was emptied, and 11.7 kg of fresh alumina was added. The material removed after the oxidation cycle was charged to the reactor for fluorination, while the alumina removed after the hydrogen chloride cycle was discarded.

Figure 7 shows the zircaloy reaction progress and the hydrogen chloride consumed during the de-cladding operation. Figure 8 shows the uranium dioxide progress and oxygen consumed during the oxidation step.

The fluorination was conducted using stepwise increases of fluorine in nitrogen from 5 to 30%.

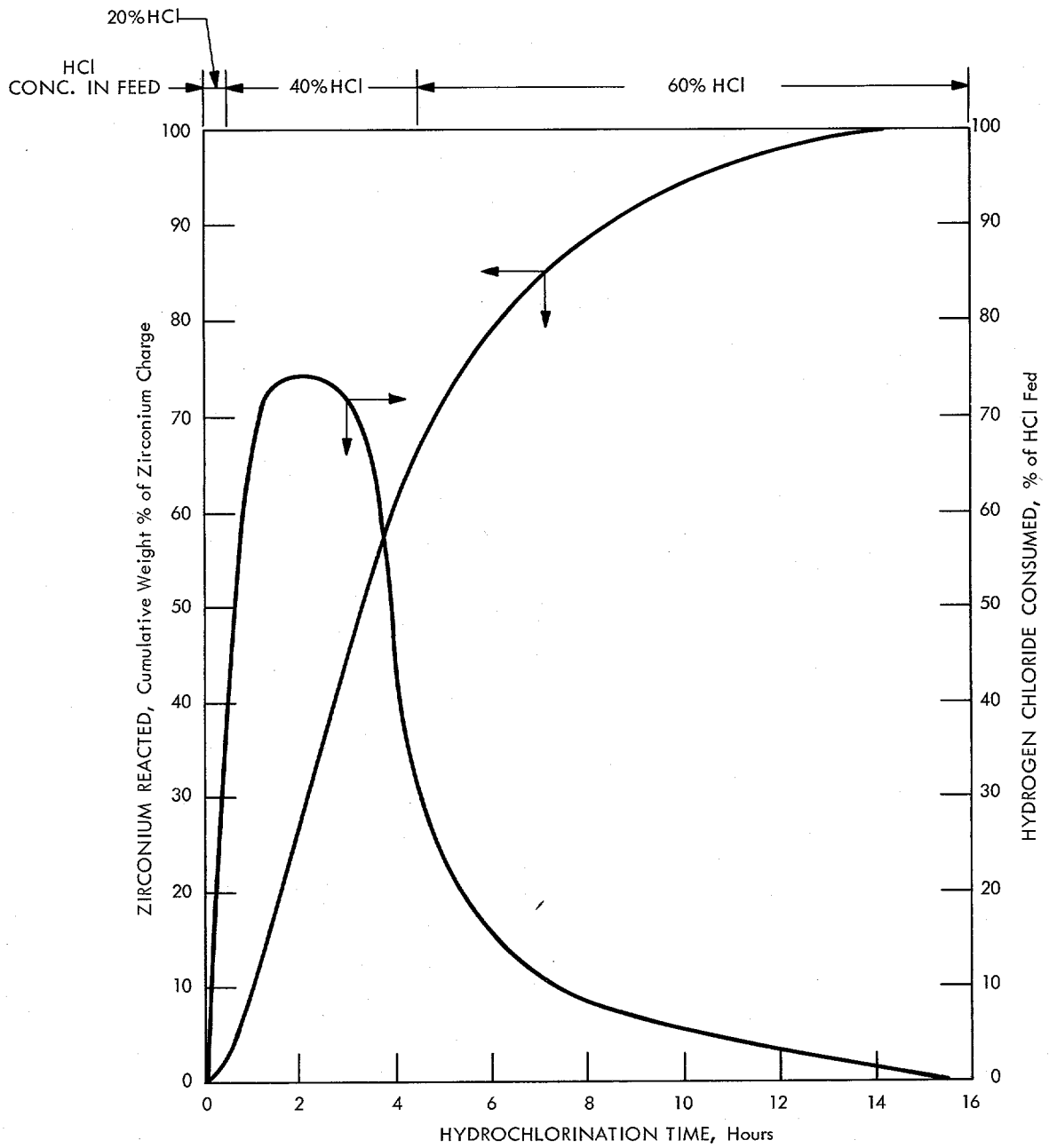
The filter cooler was operated at about 125°C, but during the first 1-1/2 hours of the cycle, the temperature in the upper section rose to about 200°C before the applied coolant reduced the temperature to the desired level.

During the oxidation cycle, 62.9 kg, which amounts to 55.7% of the reactor pellet uranium-plus-alumina charge, was elutriated. The elutriated material included 91.0% of the uranium charge and 3.5% of the reactor alumina charge and, therefore, was estimated to be 82.7% uranium; i.e., 97.5%  $U_3O_8$  equivalent. Since the elutriated material mixes with the alumina charged to the filter cooler, a correction must be applied to the total material found in the cooler and its overflow before the amount of uranium transferred can be computed from a chemical analysis.

During the fluorination cycle, 28.5 kg material containing 22.4 kg uranium was elutriated from the reactor, and 50.4 kg of uranium hexafluoride was collected in the cold traps; therefore, only 59.5% of the uranium charge was converted to uranium hexafluoride. Analysis of the reactor material after fluorination indicated that it contained only 0.15% uranium, or less than 0.1 kg of uranium. In addition, the concentration of zirconium in the bed was found to be equivalent to 2% of the zirconium in the original charge.

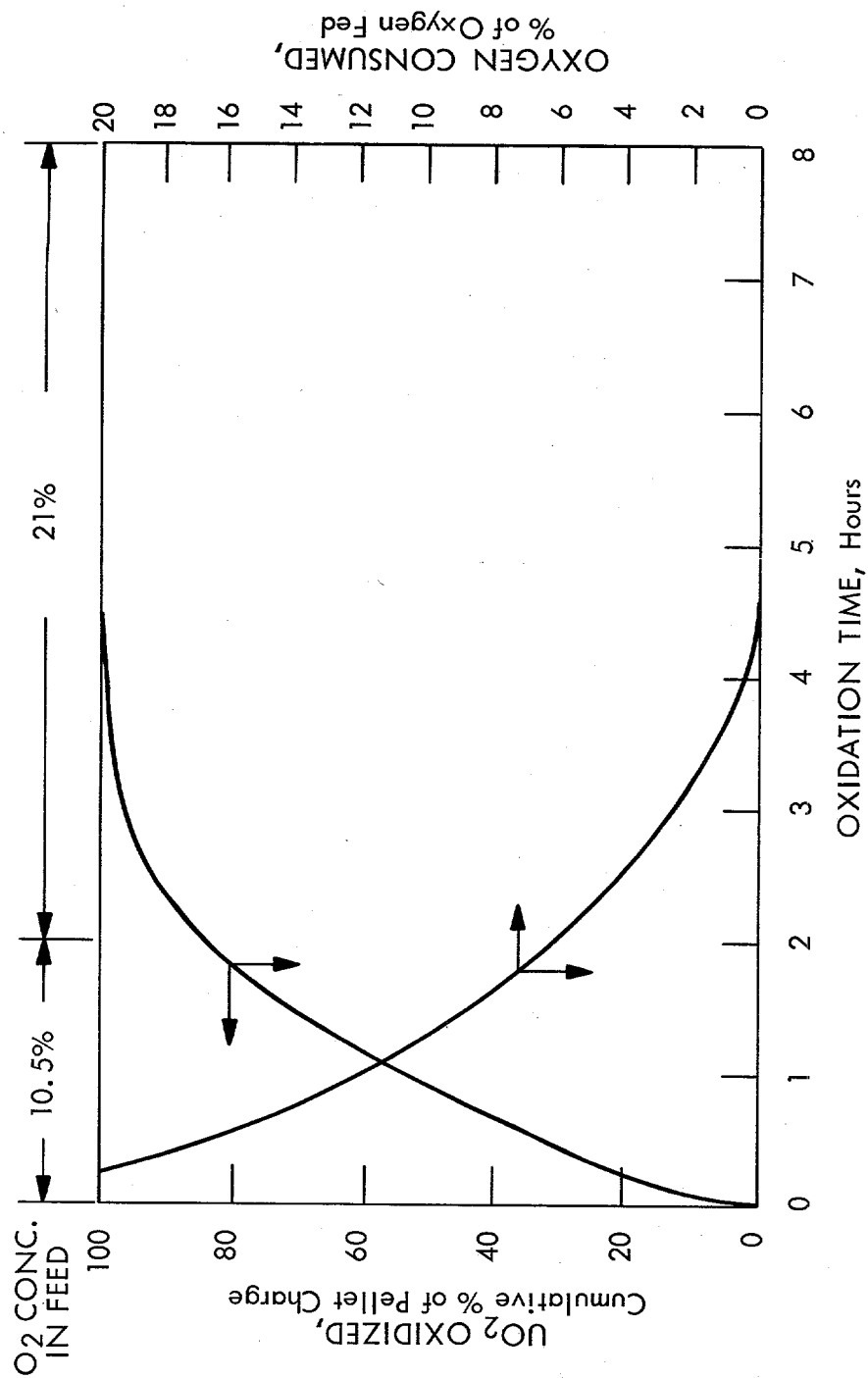
In-place flow tests were conducted at approximately 17 and 33 scfm at 315°C before the run and after the oxidation cycle. These tests showed that the pressure drop through the filters had increased from 0.1 to 8.9 psi at the lower flow and from 0.4 to 15.4 psi at the higher flow. The flow rates measured in terms of cubic feet per minute per square foot of filter surface per pound per square inch pressure drop across the filters had decreased over 97% over the course of UE-29. These tests indicate that the plugging during this run was equivalent to the combined plugging for the three previous runs which were performed without intermediate filter cleanup. At the end of the fluorination cycle, the flow rate was 0.5 cfm/sq ft-psi at a flow rate of 5.1 scfm at 120°C.

The filter tubes were removed and cleaned by vacuuming and brushing powder from the surface, followed by a warm water wash (about 65°C). The water



ZIRCONIUM REACTED AND HCl CONSUMED IN RUN UE-29

Figure 7



$UO_2$  OXIDIZED AND OXYGEN CONSUMED  
IN RUN UE-29

Figure 8

wash was accomplished by pumping water into the inside of the filters causing water flow opposite to the direction of gas flow when filtering. The tubes were flow tested in the filter flow station after the powder had been removed, and after the tubes had been washed and dried. The results indicate major flow capacity recovery, since the average flow after washing had risen to 90.8 cfm/sq ft-psi.

#### Runs UE-30 and UE-31

Two runs, UE-30 and -31, were made to check the possibility that EGCR pellets are more easily oxidized than uranium dioxide pellets from other sources. In these runs, the operations were conducted at low superficial velocities to determine if the channeling and plugging which occurred in early semiworks tests at low velocities when solid (nonannular) uranium dioxide pellets from various manufacturers were used would take place with EGCR pellets. Alumina balls were used to position the bottom of the pellet bed in the 5-inch-diameter section of the reactor 1 foot 10 inches above the bottom. The pellet bed depth was approximately 3 feet, and thus extended into the 5- to 10-inch-diameter transition section of the reactor. The alumina powder bed depth was 2 feet 3 inches in each run. The filter cooler was operated with the six filters cleaned after run UE-29.

The reactor bed and the gas preheater discharge temperatures were both 482°C. The superficial gas velocities in the 5-inch-diameter section were 1.5 and 1.0 ft/sec at 482°C and 4 psig in UE-30 and -31, respectively. The superficial gas velocity in the 10-inch-diameter section was about 0.4 ft/sec at 482°C and 2 psig in each run.

The oxidation cycle in UE-30 consisted of 2 hours at 10.5% oxygen and 7-1/4 hours at 21% oxygen. In UE-31, the cycle consisted of 3 hours at 10.5% oxygen and 9 hours at 21% oxygen. The run was continued 1 hour after the oxygen analyzer indicated no additional oxygen consumption in each case.

The bed did not plug seriously during either of the runs; however, there were some erratic inlet pressure and reactor pressure drop fluctuations similar to those observed in earlier runs with other pellets. The inlet pressure varied from 3 to 11 psig, and the bed pressure drop varied from 2 to 9 psi. Each pressure cycle, i.e., an increase and then a decrease in both reactor inlet pressure and pressure drop, was accompanied by an increase and decrease in oxygen consumption. There was no large increase in pressure drop across the filters during either run. The flow rate capacity of the filters after UE-31 was measured by in-place tests with 16.7 and 34.8 scfm flow to be 3.8 and 5.6 cfm/sq ft-psi, respectively. In UE-30, 3.3 kg of plus 35-mesh material remained after oxidation, and in UE-31, 3.0 kg of plus 35-mesh material remained after oxidation. The pressure fluctuations in each of these runs indicated a tendency to channel and to plug, and the amount of plus 35-mesh material in the reactor at the end of the test and the long times required for oxidation, i.e., 9-1/4 and 12 hours for UE-30 and -31, respectively, as compared to the usual 6-1/2 to 8 hours, indicate poor mixing of the U<sub>3</sub>O<sub>8</sub> powder formed with the fluid bed of alumina. It must be noted, however, that the

tendencies to plug, etc., were much less severe in these runs than in the earlier runs, UE-7 through -12, with other uranium dioxide pellets. This difference may be attributable to the lower bulk density of the EGCR pellets, 4.9 g/cc as compared to about 5.8 g/cc for the other pellets, or possibly to the annular nature and somewhat larger size of the EGCR pellets.

The total oxidation time in the runs, 9 and 12 hours, was longer than required to oxidize 65 kg of EGCR pellets in shallow beds in the 10-inch-diameter section of the reactor. In addition, some of the remaining bed material was in the form of whole or half-size pellets, and overall comminution was barely acceptable.

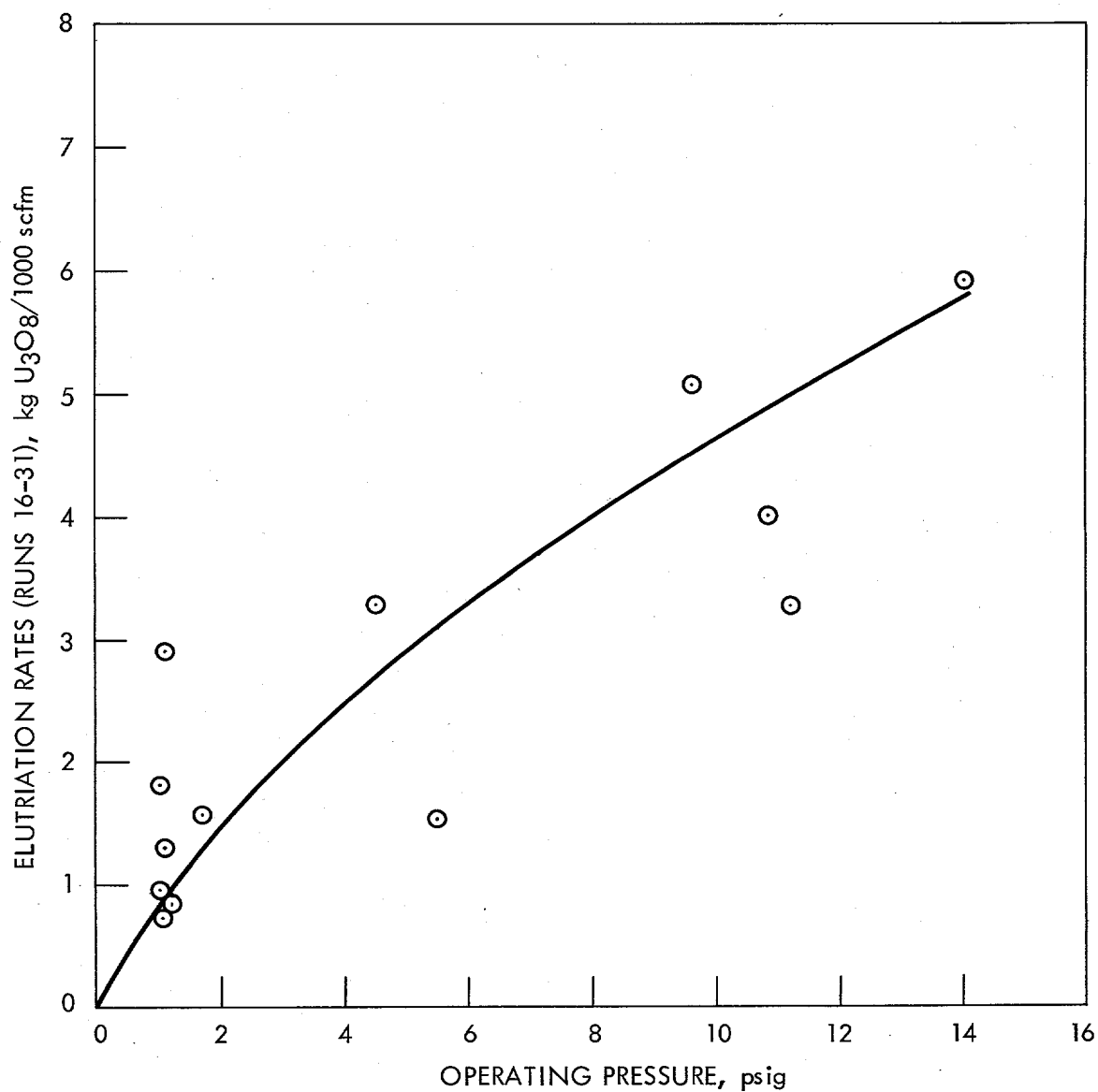
The elutriation rates in these runs were considerably lower than in runs UE-25 to -29. In UE-29, 29.3% of the pellet-plus-alumina charge was elutriated, and in UE-31, 10.8% of the pellet-plus-alumina charge was elutriated. In figure 9, the  $U_3O_8$  elutriation rates for runs UE-16 through -31 have been plotted versus the operating pressure. Runs UE-25 through -29 were carried out at pressures over 4 psig, and as can be seen in the graph, the elutriation rates have been high; i.e., 3.25 to 5.9 kg  $U_3O_8$  per 1,000 scfm of gas. Of course, in these runs, the development of this high a pressure was concomitant with a declad phase operation preceding oxidation. The pressures during runs involving oxidation only have been about 1 to 1-1/2 psi, and elutriation rates have averaged about 1-1/2 kg  $U_3O_8$  per 1,000 scfm.

The conclusions reached from the test results are as follows:

#### 1. Decladding Tests

- a. Decladding, with charges containing up to 23 kg of zirconium and/or zircaloy, can be controlled successfully in the semiworks system using hydrogen chloride concentrations increased stepwise over the course of the run from 20 to 60%. Most of the metal is consumed. There appears to be no adverse effect of the hydrogen chloride treatment on the subsequent oxidation reaction, although there may be an influence on  $U_3O_8$  elutriation rate.
- b. The semiworks equipment, with the exception of the nickel filters, appears suitable for zircaloy decladding runs using hydrogen chloride. The permeability of the filters decreases markedly after a few cycles of exposure to the off-gases from the declad reaction.
- c. Some of the flow capacity of the exposed filter can be regained by mechanical removal of the powder coating; however, a back-flush of water is apparently necessary to restore very much of the original permeability. Unfortunately, after this treatment, the filters appear to be more readily susceptible to plugging. The six filters used in UE-28 were cleaned and reused in UE-29. The plugging during the latter run was as great as the total





$U_3O_8$  ELUTRIATION RATE AS A FUNCTION OF PRESSURE

Figure 9

plugging for the run series UE-26 through -28, during which the filters were not cleaned.

## 2. Oxidation Tests

- a. Oxidation of uranium dioxide pellets to form  $U_3O_8$  powder can be conducted successfully in the semiworks plant. The reaction can be controlled, and the off-gas cooling and filtering facilities are adequate.
- b. A minimum superficial gas velocity through the EGCR pellet bed must be maintained in order to keep the reacting bed free of the powder produced. This minimum velocity is dependent on the depth of the pellet bed. For a shallow bed (up to about 1 foot high), a velocity of 1 ft/sec appears to be satisfactory, although some powder buildup can probably be tolerated. For deeper beds, it appears that the minimum velocity required is greater than 2 ft/sec, with 3 ft/sec being definitely sufficient.
- c. The technique of oxidizing the pellet bed from the top (runs UE-16 through -21) has been effective in reducing the tendency of the bed to plug or channel.
- d. Stepwise increases of oxygen concentration in nitrogen from 5 (or 10) to 21% over the course of a run are effective in controlling the uranium dioxide oxidation rate. The technique can be used successfully for oxidation runs with shallow beds of EGCR pellets (and probably shallow beds of other types of pellets) at fluidizing velocities as low as 1 ft/sec without the necessity of forcing the reaction to occur from the top of the bed in order to avoid bed plugging.
- e. Oxidation of the 3/4-inch annular type EGCR pellets can probably be accomplished with lower superficial gas velocities than were required when oxidizing the smaller solid cylindrical uranium dioxide pellets used in runs UE-1 through -15. The EGCR pellets were successfully oxidized in runs UE-30 and -31 in a 3-foot-deep pellet bed at 1.5 and 1.0 ft/sec, respectively. Although there was a tendency for the bed to plug during the oxidation, both runs were completed. Comminution\* of the uranium dioxide

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\* Comminution is, of course, defined as percentage of uranium material passing a 35-mesh screen after the oxidation step, while depending in part on the flow sheet. Comminution probably should be in excess of about 95% to be satisfactory for fluorination in a one-reactor line; although, if the oversize is not much bigger than 35 mesh, more might be tolerated. An elutriation flow would require essentially 100% comminution; however, some of the material might be held over as a heel to be broken up in the next cycle.

was about 95% and the conversion to  $U_3O_8$  based on chemical analysis averaged 98%. The comminution in the EGCR runs at 2 to 3 ft/sec has been approximately 95 to 99%. A velocity of 3 ft/sec was used in UE-14 and -15 to prevent channeling or plugging in a 17-inch-deep bed of the solid pellets. While 3 ft/sec may not be the minimum velocity for this type of pellet, 1.5 ft/sec probably is too low based on the results of runs UE-7 and -9. Plugging was encountered during those runs, and operations had to be discontinued at about 70% comminution. In run UE-9, the percentage conversion was only 84% based on chemical analysis. The better performance with the EGCR material may be due to the annular design of the pellets; the bulk density of a bed of pellets is only 4.9 g/cc for the EGCR material as compared to 5.8 g/cc for solid pellets. Differences in the uranium oxide properties may also exist for the various materials.

- f. In early tests (runs UE-16 through -24), the maximum amount of uranium elutriated from the reactor was about 32% of the uranium charge. Higher elutriations (55 to 94% of the uranium charge) were attained during pellet oxidation in runs UE-25 through -29.  $U_3O_8$  elutriation rates have also been higher during the deoxidation tests. Of course, coincident with the increase was the introduction of zircaloy into the system and higher operating pressures because of filter plugging tendencies. It is not known if one or both of these factors influenced the improved elutriation qualities. In general, selectivity (the elutriation of  $U_3O_8$  rather than alumina) has been acceptable; the material transferred has averaged about 85%  $U_3O_8$  during UE-16 through -31 with the highest concentrations (92 to 100%  $U_3O_8$ ) in the latter four tests. Eventual transfer of alumina to waste at an alumina-to-uranium ratio considerably higher than this would probably be required in any event to dilute the fission product content.

### 3. Fluorination

- a. From the performances in runs UE-22, -23, and -29 using elemental fluorine, the equipment appears suitable for the fluorination operation. Before bromine pentafluoride can be used, additional equipment must be added to the system so that the bromine pentafluoride can be regenerated, removed from the uranium hexafluoride, and recycled.

The heat release with fluorine is greater than with bromine pentafluoride. Therefore, control of the operating temperatures when fluorine is used would be indicative of successful reactor performance with bromine pentafluoride. Reaction temperatures during routine operations can be controlled by passing cooling air through the tubing attached to the reactor walls and by adjustment of the fluorine content of the fluidizing gas.

- b. Volatility plant designs may have to allow for the elutriation of unreacted  $U_3O_8$  from the main reactor to the filter cooler

during fluorination. Large amounts of the oxide were transferred during processing with elemental fluorine in runs UE-22, -23, and -29. The amount elutriated may be different with bromine pentafluoride, especially with somewhat lower operating temperature possible with this reagent. If necessary, the filter could be located directly above the reactor (however, this might interfere with charging in a single-vessel process) or special equipment, such as a cyclone in the off-gas line from the reactor and a device for pneumatic transfer of collected solids, could be provided for return of the elutriated material to the main reactor.

#### Bench-Scale Elutriation and Fluidization Studies

Another in a series of small-scale tests has been made to investigate the elutriation properties of the  $U_3O_8$  product of the semiworks fluid-bed oxidation step. Separation of the  $U_3O_8$  from the alumina diluent used in the fluid bed is potentially desirable in a plant to allow transfer of the oxidation product to a second reactor for fluorination while retaining most of the alumina in the first reactor for use in the subsequent dechlorination and pellet oxidation operations. The elutriation column employed was a 7-1/2-foot-long, 2-inch-Plexiglas tube. Air at ambient temperature was injected in the bottom of the column for fluidization, and the freeboard above the expanded fluidized bed amounted to about 1-1/2 feet. Elutriated material was collected on a sintered metal filter mounted in a separate filter case.

Tests were conducted using alumina- $U_3O_8$  mixtures taken from the minus 35-mesh fraction of the reactor beds after semiworks oxidation runs UE-17 and -20. The charges analyzed nominally 19% and 76%  $U_3O_8$  in alumina; therefore, the studies involved both relatively low and high  $U_3O_8$  concentrations. The amounts of  $U_3O_8$  and alumina transferred are shown in table XXII, while the concentrations in the column beds over the course of the runs are plotted in figures 10 and 11.

In the tests with the lower concentration charge, 91 to 92% of the  $U_3O_8$  was transferred at velocities from 1.0 to 2.5 ft/sec; with the high concentration charge, the amount of elutriated  $U_3O_8$  ranged from 87 to 96% of the original  $U_3O_8$  loading. In general, the rate of transfer of both  $U_3O_8$  and the alumina tended to increase with increased velocity.

Figure 10 indicates the existence of an apparent minimum  $U_3O_8$  bed concentration for the tests with the lower concentration charge. When figure 11 is replotted in terms of bed weight ratio of  $U_3O_8$  to alumina versus elapsed time, portions of the plot are relatively linear, thus indicating a constant rate of  $U_3O_8$  elutriation for considerable ranges of high bed concentrations.

Whether this small residue represents a nonelutriable heel which would build up on successive oxidations and elutriations is not known. The curves also indicate that the elutriation rate is influenced by the  $U_3O_8$  concentration in the fluidized bed. It was noted visually that, during periods of high  $U_3O_8$  bed concentration, i.e., greater than about 50%

TABLE XXII  
RESULTS OF ELUTRIATION TESTS

Test No.	Gas	Elutriation Time, hr	$U_3O_8$	$Al_2O_3$
	Superficial Velocity, ft/sec		Transferred, Percentage of Original Charge	Transferred, Percentage of Original Charge
Test Series I: Using the bed from semiworks oxidation run UE-17 (nominally 19% $U_3O_8$ in alumina*)				
1	1.0	1.0	91	0
2	1.5	1.0	91	1.7
3	2.0	2.0	91	3.6
4	2.5	0.5	92	6.6
Test Series II: Using the bed from semiworks oxidation run UE-20 (nominally 76% $U_3O_8$ in alumina**)				
1	1.0	7.0	87	9.8
2	1.5	5.0	95	24
3	2.0	4.2	92	25
4	2.5	2.3	96	22
* Analyses of the test charges indicated some variation from the nominal value with the range being 17.5 to 21.6% $U_3O_8$ .				
** Analyses of the test charges indicated some variation from the nominal value with the range being 75.5 to 78.4% $U_3O_8$ .				

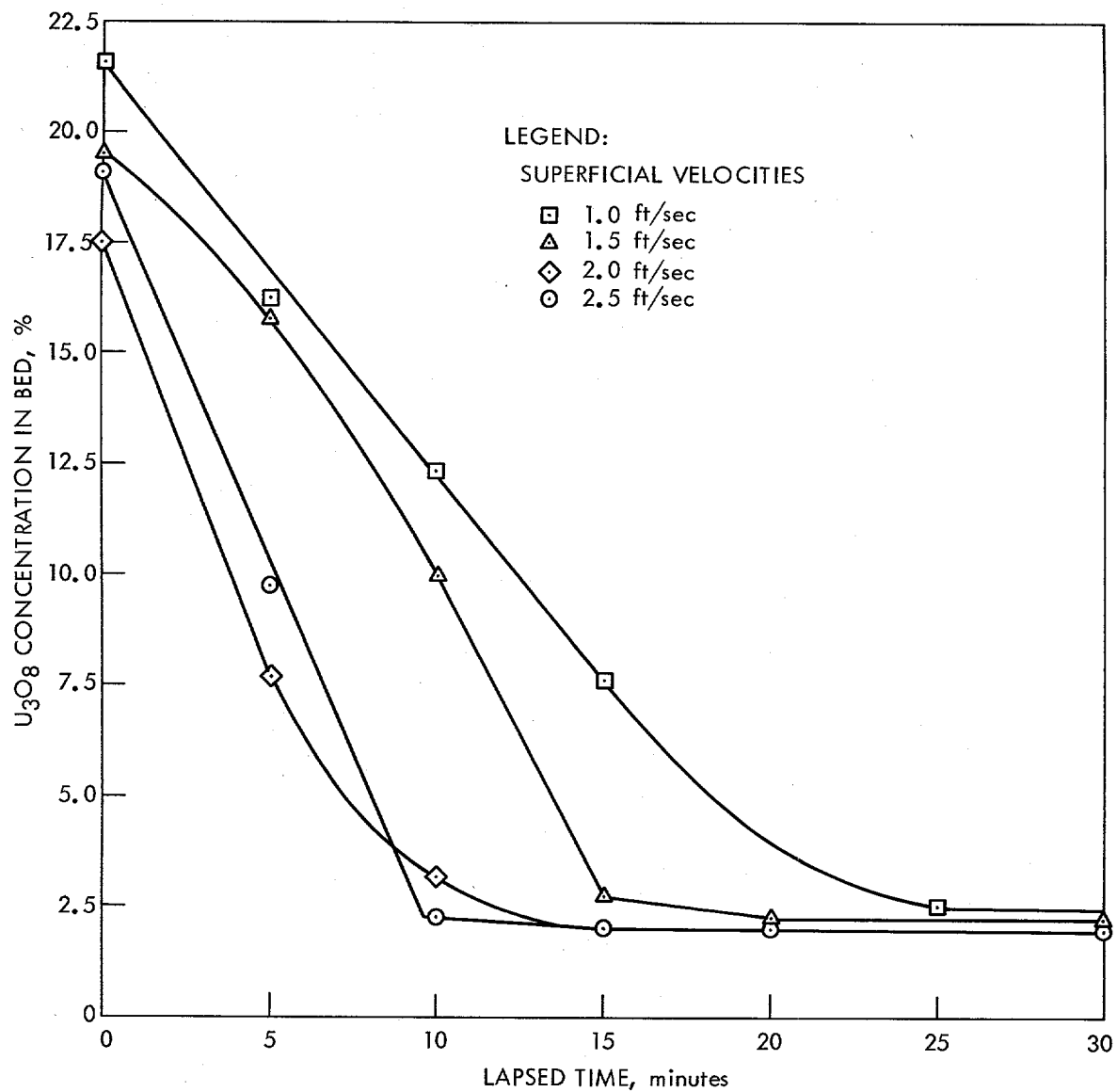
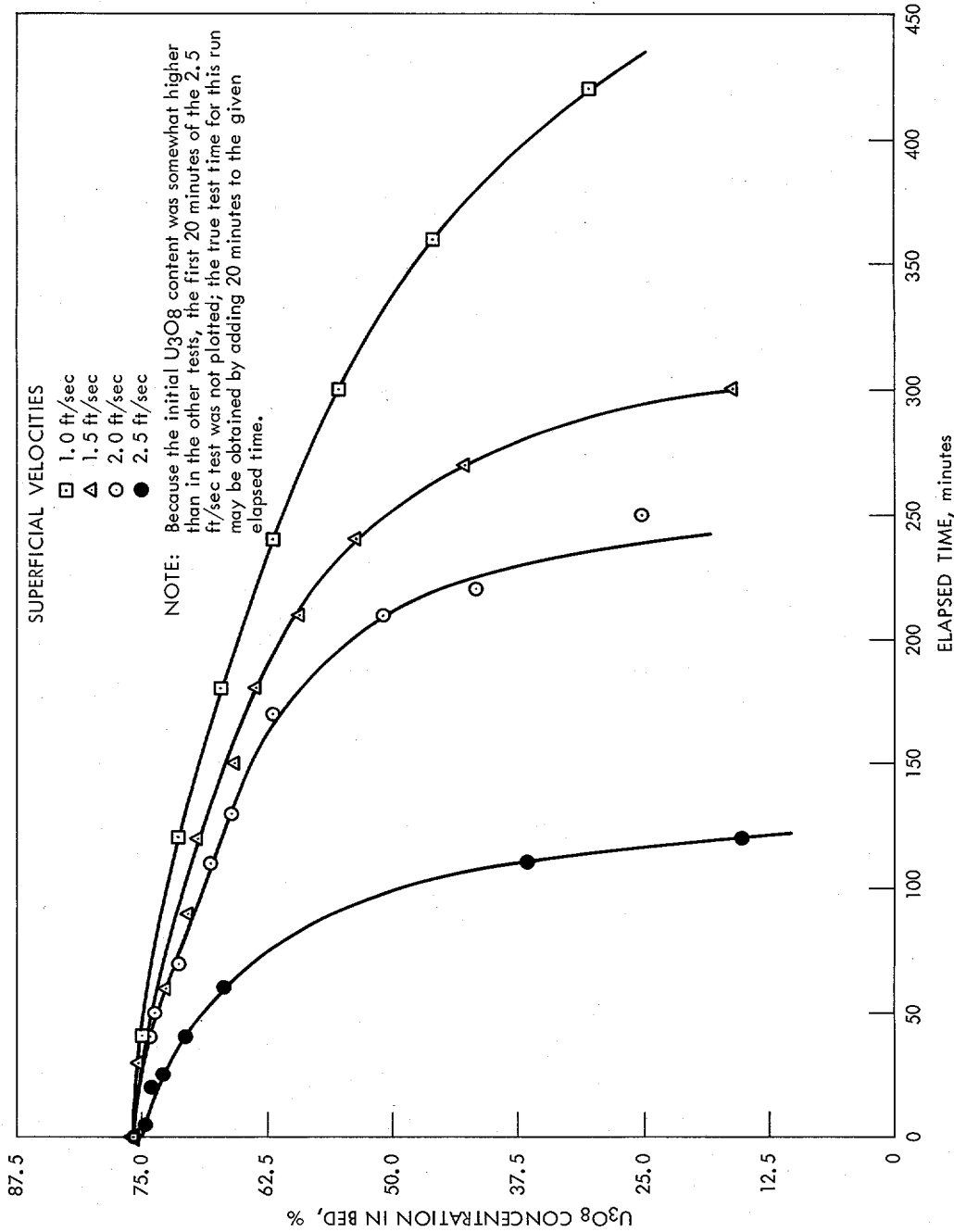


Figure 10  
ELUTRIATION OF  $U_3O_8$  FROM  $U_3O_8$ -ALUMINA MIXTURES  
( $U_3O_8$  concentration in mixture is a nominal 19%)

DWG. NO. G-68-102



ELUTRIATION OF  $U_3O_8$  FROM  $U_3O_8$ -ALUMINA MIXTURES  
( $U_3O_8$  concentration in mixture is a nominal 76%)

Figure 11

$U_3O_8$ , agglomerates formed in the freeboard volume of the column and dropped back into the fluidized bed. With lower bed concentrations, agglomeration was not observed. Similar agglomerates have been noted previously during screening operations. Their formation is probably due to electrostatic charges on  $U_3O_8$  fines which are present in the bed.

An examination of these data indicates that a bed velocity of about 2 ft/sec may be optimal for this type of material at atmospheric pressure, considering both the rate of  $U_3O_8$  entrainment and the percentage of alumina transferred.

### SAMPLING

In the fluoride volatility process, it will be necessary to sample solids accurately for accountability purposes when such solids are being transferred from one location to another; e.g., from reactor to waste disposal or possibly between vessels in a multiple vessel process. Previous reports have contained the results of sampling tests with a 6-inch Denver Vezin solids sampler through which 1/8-inch-diameter pellet mixtures or mixtures of 20- to 40-mesh quartzite powder and relatively fine 60- to 325-mesh sodium fluoride were fed. The particle sizes for the powders were chosen to permit the use of screening to analyze sample cuts. The data for the powder mixtures, although limited, suggested the presence of small sampling biases (about 0.24 to 1%), the direction of which, i.e., the preferential sampling of one size over the other, was related to the feed rate to the equipment.

Mixtures of  $U_3O_8$  and tabular alumina have now been passed through the sampler at various feed rates, and sampler performance was checked by chemical analyses. A collected sample was thoroughly mixed prior to removing a small portion for laboratory analysis. The reject stream and the remainder of the collected sample were then remixed for repass through the equipment in the next experiment. The results of the tests are shown in table XXIII.

In run series 1 and 2, a measured concentration of 27.6%  $U_3O_8$  was used, and in run series 3 and 4, the concentration of  $U_3O_8$  was 70.0% by weight. The data show that an average sample cut of 5 to 5.5% was experienced in all runs. The sample cut appeared to be affected at most only slightly by throughput rates and densities.

The following mean values were obtained for the four runs with the limits of error quoted being at the 95% confidence level.

Run 1	27.69 $\pm$ 0.54%
Run 2	27.63 $\pm$ 0.57%
Run 3	68.99 $\pm$ 0.73%
Run 4	69.41 $\pm$ 0.60%



TABLE XXIII  
SAMPLER TEST DATA

Run No.	Total Weight Fed, lb	Weight of Sample, lb	Sample Cut, %	Time Required, min	Feed Rate, lb/hr	Sample Analysis U <sub>3</sub> O <sub>8</sub> , %
1a	144.1	7.9	5.5	22.2	389	27.94
b	144.0	8.0	5.6	21.6	399	27.81
c	144.0	8.0	5.6	21.5	401	27.82
d	143.9	8.0	5.6	22.2	389	27.18
2a	143.9	7.6	5.3	1.15	7500	27.75
b	143.9	7.5	5.2	1.11	7810	27.28
c	143.7	7.4	5.1	1.11	7800	27.42
d	143.7	7.6	5.3	1.10	7810	28.08
3a	150.0	7.9	5.3	17.67	509	68.92
b	150.0	8.2	5.5	15.28	587	69.62
c	149.9	8.0	5.3	20.10	447	68.88
d	149.7	8.3	5.5	16.98	529	68.52
4a	149.7	7.9	5.3	1.93	4650	69.97
b	149.4	7.9	5.3	1.90	4720	69.10
c	149.4	7.8	5.2	1.77	5070	69.34
d	149.4	7.5	5.0	1.92	4680	69.23

A comparison of the true mean versus the statistical averages in runs 1 and 2 indicated that representative samples of the mix were taken, and no bias is present. In the higher  $U_3O_8$  concentration, runs 3 and 4, a small bias may exist.

Four control samples taken from a blended sample at each concentration were submitted to the laboratory to check the deviation due to analytical techniques. The analytical results were determined to be  $27.55 \pm 0.83\%$  and  $69.03 \pm 0.12\%$ . The analytical deviations estimated from the control analyses suggest that the sampler may be somewhat more accurate than indicated by the above evaluation.

#### OUTLET GAS FILTER STUDIES

Sintered nickel fiber filter tubes, 3 feet long, manufactured by the Huyck Metals Company, have been exposed in the filter test loop to hydrogen chloride-zirconium tetrachloride-stannous chloride-inert gas mixtures typical of the off-gases produced during the decladding of zircaloy-clad power reactor fuels. This exposure has been followed by treatment with dilute oxygen to simulate the uranium dioxide pellet oxidation and then with dilute fluorine to simulate the fluorination portion of the processing cycle. In preliminary studies, air flow tests on the filter tubes before and after exposure, have indicated permeability losses on the order of 85% for three exposure cycles, as compared to previously determined filter permeability decreases of about 30% for multicycle exposures to the off-gases from identical chemical treatments without zircaloy.

One explanation of the additional plugging has involved formation of a complex salt by the interaction of zirconium tetrachloride with the filter media. The filter permeability has been largely recovered by treatment with 10 to 15% hydrogen at  $540^\circ\text{C}$ .

Basic operating conditions for the filter loop test runs conducted during the current report period are summarized in table XXIV. Simulated decladding off-gas mixtures were prepared by reacting zircaloy-2 at  $400^\circ\text{C}$  with hydrogen chloride. The reaction was carried out for 8 hours in the filter loop reactor with a charge of 0.9 kg of the metal alloy in about 7 kg of 48- to 100-mesh tabular alumina. The reactor superficial gas velocity during hydrochlorination was maintained at 0.75 ft/sec. The off-gases from the reactor pass through the filter under test.

Hydrogen equivalent to 30% by volume was added to the hydrogen chloride used in all the tests on the theory that the plugging reaction might be inhibited during decladding, even though the operating temperature ( $310$  to  $370^\circ\text{C}$ ) would be low compared to the  $540^\circ\text{C}$  at which the successful separate hydrogen treatments were conducted. In processing plant decladding operations, hydrogen concentrations may be 30%, or even higher if the reactant gas stream is recirculated.

The oxidation phase consisted of exposing the filter to 15% oxygen at  $100^\circ\text{C}$  for 10 hours. When used, the fluorination conditions involved an

TABLE XXIV  
BASIC OPERATIONAL CONDITIONS FOR FILTER LOOP TESTS

Conditions	Run Number										
	1	2	3	4	5	6	7	8	9	10	11
Type of Filter Tested											
Makeup of Reactor Charge*:											
Zircaloy-2	X	X	-	-	-	-	X	X	X	X	-
Alumina	X	X	X	X	X	X	X	X	X	X	X
Zirconium	-	-	-	-	-	-	-	-	-	-	X
Hydrogen Chloride Supplied, vol %	30 to 70†	30 to 70†	30 to 70†	30 to 70†	30 to 70†	10 to 70§	10 to 70§	10 to 70§	10 to 70§	10 to 70§	10 to 70§
Filter Temperature During Decladding, °C	343	370	370	315	310	310	310	310	315	315	315
Process Phases in Cycle**:											
Decladding	X	X	X	X	X	X	X	X	X	X	X
Oxidation	X	X	X	X	X	X	X	X	X	X	X
Fluorination	X	X	X	X	-	-	-	-	-	X	X
Number of Cycles In Run	1	1	1	1	1	1	1	1	5	4	6

\* Charge Size: 0.9 kg of zircaloy-2 or zirconium and 7 kg of alumina.

+ Hydrogen chloride concentrations of 30, 50, and 70% were used in runs 1 through 5 for 2-, 3-, and 3-hour exposures, respectively. Sufficient hydrogen was added to maintain 30 volume percent in the reactor off-gases. Argon was used as diluent.

§ The hydrogen chloride concentration was started at 10% and increased 10% each hour to a maximum of 70% in runs 5 through 11. Sufficient hydrogen was added to maintain 30 volume percent in the reactor off-gases. Argon was used as diluent.

\*\* Superficial gas velocities: 0.75 ft/sec during decladding and 1.0 ft/sec during oxidation and fluorination. The oxidation was conducted with 15% oxygen and fluorination with 20% fluorine.

exposure to 20% fluorine at 100°C for 10 hours. A superficial velocity in the reactor of 1.0 ft/sec was used for both the oxidation and fluorination phases.

Run summaries are as follows:

#### Runs 1 Through 8

Single cycle filter loop tests were conducted to evaluate the influence of gas concentration and filter temperature on filter plugging. A used Huyck filter, 85% plugged, was employed for the first four runs, but a new filter was tested in runs 5 through 8. Test results are shown in table XXV. The decladding, oxidation, and fluorination steps were conducted for run 1, with the filter maintained at 343°C during decladding off-gas filtration. The hydrogen chloride concentration was started at 30%, then increased to 50%, and finally to a maximum of 70% to complete the declad step. The filter permeability loss rose to 90% during the hydrochlorination and the pressure drop across the filter increased 0.4 psi over the course of the full run\*. The filter temperature was increased to 370°C in run 2. The filter pressure drop increased 2.1 psi during the decladding phase. On completion of the 8-hour hydrochlorination, the filter was exposed to 30% hydrogen in argon at 370°C for 2 hours, resulting in a 1.5 psi decrease in filter pressure; i.e., 0.2 psi higher than prior to hydrochlorination.

This test was repeated in run 3, except that no zircaloy charge was used. As expected, the permeability loss was considerably less than under similar conditions wherein the zircaloy reaction products were present. This test was again repeated in run 4 without zircaloy. The filter temperature was reduced to 315°C during decladding, and there was no increase in on-stream pressure drop across the filter over the course of the run.

In run 5, a new nickel fiber filter was installed in the test loop and exposed to declad reaction off-gases produced in the absence of zircaloy-2. The fluorination phase of the cycle was omitted, on the theory that the presence of fluoride might in some way be the cause of the abnormal plugging. Such an operation would be feasible in the plant process if a two-reactor vessel system was employed. Very little plugging developed during this run.

In runs 6 and 7, the hydrogen chloride exposure conditions were changed. The hydrogen chloride concentration was started at 10% and increased 10% each hour to a maximum of 70% to reduce the partial pressures of the volatile zirconium and tin compounds and thereby to reduce the possibility of desublimation on the filter surface. The reactor bed was removed and screened following these runs. Less than 30 grams of plus 35-mesh

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\* The pressure drop across the filters due to gas flow is less than 0.05 psi in these tests. The pressure drop is this low because the standard filter employed is somewhat oversized in relation to the flow through the test bed.

TABLE XXV

## RESULTS FOR SINGLE CYCLE TESTS IN FILTER LOOP USING NICKEL TUBES

Run Results	Run Number							
	1a	2a	3ab	4ab	5bc	6c	7c	8c
Change in Pressure Drop Across Filter, psi:								
During Run	+ 0.4	+ 2.1	+ 0.7	0	+ 0.02	+ 0.1	+ 0.06	+ 0.6
After Separate Treatment with 30% hydrogen		- 1.5						0
Estimated Cumulative Plug After Hydrochlorination, %:								
Directly After Hydrochlorination	90	-	90	94d	-	82	-	-
After Subsequent Separate Treatment with 30% Hydrogen	-	90	-	-	-	-	-	93

a A used filter tube, which was already plugged 85%, was used for the first run. The filter was then in service for runs 1 through 4 in sequence.

b No zircaloy charged.

c A fresh filter tube was installed for run 5. The filter was in service for runs 5 through 8 in sequence.

d This value was calculated from laboratory flow data. All other plug figures are based on on-site test loop data taken using argon with the filter at room temperature.

material was found, with most of this coarse material being spalled fragments from the alumina balls which had been used as the bed support.

Although operating conditions for run 8 were the same as 6 and 7, the resultant filter pressure drop increase was considerably greater. About one-half of the permeability loss was recovered by treating with 30% hydrogen at 315°C for 2 hours after completion of the hydrochlorination step. The filter was also exposed to 30% hydrogen at 425°C following the oxidation phase, with no change in pressure drop resulting.

The test series indicated that the presence of excess hydrogen in the dechlorination off-gases does not prevent plugging or even substantially reduce the plugging rate at the operating filter temperatures. On the other hand, a separate treatment after dechlorination using hydrogen diluted with argon at temperatures as low as 315°C was effective in decreasing the plug. Possibly the presence of excess hydrogen chloride at the conclusion of the dechlorination cycle prevented regain of filter permeability. The filter plugging also appeared to increase directly with filter temperature, as noted by the 1.5 psi rise in the pressure differential across the filter at 370°C during run 2, as compared with the 0.4 psi rise during run 1 when the filter temperature was 343°C.

#### Run 9

Inconel could also be an acceptable filter material for the hydrochlorination and oxidation cycles in a two-reactor vessel system. In test loop run 9, zircaloy-2 was changed to the reactor and a filter tube constructed of sintered Inconel was exposed to five cycles of hydrochlorination-oxidation. The pressure differential across the filter increased about 0.1 psi during each hydrochlorination. The increase was cumulative. Laboratory flow measurements indicated a 75% loss of flow capacity as a result of the five-cycle exposure. In comparison, an 80% capacity loss was previously noted when Inconel filter tubes were exposed to 19 cycles of hydrochlorination-oxidation-fluorination atmospheres without the cladding volatiles. The 75% permeability loss was considerably lower than the 82 to 94% experienced with sintered nickel fiber tubes exposed under similar conditions in runs 1 through 8. The comparison may, however, be somewhat biased, since the original porosity of the Inconel tube was about 1-1/2 times that of the nickel fiber unit.

#### Run 10

The test loop was altered to permit operation of two filters in series, measurement of internal filter temperatures, and filter blowback with heated argon. The series arrangement allows simultaneous performance testing of filters with and without reactor bed material dust collecting on the surface.

In run 10, two new sintered nickel fiber filters were installed in the test loop and fluorinated with 50% fluorine in nitrogen for 5 hours at 260°C before exposure to hydrogen chloride. It was hoped that this treatment might at least slow down the buildup of any nickel chloride

and/or zirconium tetrachloride complex that might be involved in the filter plugging observed during the hydrochlorination phase of the filter exposure cycle. The fluorinated filters were then exposed to cycles of off-gases from zircaloy-2 decladding, oxidation, and fluorination, each of which was conducted according to methods previously described.

Little change in operational filter pressure drop was noted until the third cycle. During the hydrochlorination phase of this cycle, the plugging of the primary filter increased significantly as indicated by a rise in pressure drop from 0.02 to 0.5 psi. This pressure differential increased to more than 5.0 psi during the first 5 hours of the fourth cycle hydrochlorination. The test was interrupted, and the primary filter pressure drop was reduced to 2.5 psi by exposing the tube to 30% hydrogen in argon for 1 hour at 350°C. The hydrochlorination phase was then successfully completed.

Temperature excursions were observed on both tubes during the fluorination phases of all four cycles, and consequently, the fluorine was added intermittently during the first 30 minutes of this portion of each cycle. By this technique, filter temperatures were maintained at about 350°C maximum during the fluorination reactions with the exception of one short temperature excursion to 500°C.

In an inspection of the filter tubes at the completion of four cycles of operation, both units were found to be coated with a white powder less than 1/32 inch thick. The end cap weld on the secondary filter had been severely attacked, and there was an opening about 1/16 inch wide about half-way around the circumference which allowed sufficient leakage to account for the low pressure drop measurements for this unit during the tests.

Laboratory flow measurements made on the primary tube before and after the four-cycle exposure showed that over 99% of the flow capacity had been lost; however, the tube retained sufficient porosity to pass 0.8 scfm of air per square foot of surface area per pound per square inch pressure drop. A small section of the secondary filter was flow tested, and a flow capacity loss of about 99% was indicated for this filter also.

Analysis of the filter coatings by wet chemical methods indicated the presence of zirconium, nickel, and aluminum, with compositions as follows:

	<u>Primary Filter,</u> <u>weight percent</u>	<u>Secondary Filter,</u> <u>weight percent</u>
Zirconium	8.71	6.99
Aluminum	38.70	21.40
Nickel	1.30	4.07
Undetermined*	51.29	67.54

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\* Anionic elements such as fluorine and oxygen undoubtedly account for most of this fraction.

Analysis by X-ray diffraction of the coating on the primary filter indicated the presence of 60% alumina plus 40% unknown, while the secondary filter coating gave diffraction patterns that could not be specifically identified using available standards. Electron microprobe examination of the secondary filter coating indicated that zirconium, fluorine, and oxygen were present.

Samples of the powder from the secondary filter were heated in air for 1 hour at each of the following temperatures: 200, 400, 600, and 800°C. The powder heated to 200°C produced an unidentifiable X-ray diffraction pattern which was different from that produced by the unheated sample. The 400°C heating produced still another unknown pattern but some crystalline zirconium dioxide was also found in the sample. An incipient chemical change was thus indicated. Further conversion to zirconium dioxide was evident in the 600°C powder, and full conversion was apparent in the 800°C sample.

One of the spacing lines in the unidentifiable X-ray diffraction patterns for the room temperature, the 200, and the 400°C samples was identical to the strongest line in the zirconium tetrafluoride crystal pattern. There were, however, no other spacing line similarities between zirconium tetrafluoride patterns and the unknowns. The one spacing line similitude suggests, strictly by conjecture, that zirconium tetrafluoride may have been originally present in the filter coating, but the presence of other chemically bonded atoms produced a modified lattice structure. When the samples were heated in air, pyrohydrolysis may have taken place to convert the zirconium compound to the oxide. All this information further supports the theory that volatile zirconium compounds produced by the hydrochlorination are either collecting on the filter or reacting with it, after which oxidation and fluorination treatments are producing a nonvolatile compound, such as zirconium oxyfluoride or zirconium tetrafluoride, which plugs the filter.

#### Run 11

Testing was then continued in run 11 using zirconium metal instead of zircaloy in the charge to establish whether the minor constituents of the alloy contributed significantly to the plugging effect. Two new sintered nickel fiber tubes were installed in the test loop and fluorinated at the same conditions as noted for the previous tube fluorination.

The subsequent test exposure cycle was the same as was used with the zircaloy charges except, of course, that a 0.9 kg charge of zirconium metal was used. At the conclusion of six cycles of treatment, the filters were removed for inspection and permeability measurements. Both filters were coated with a layer of gray powder about 1/32 inch thick. Flow testing showed 75 and 85% permeability losses for the primary and secondary filters, respectively. Plugging in this test, although still relatively high, was therefore less than that incurred in tests with zircaloy. These tubes will be reinstalled in the loop for additional cycles of operation with zirconium metal to complete this test.



In runs 10 and 11, the secondary filter plugged sufficiently to indicate that at least one volatile species is involved in the loss of permeability. A permeability loss of 95% is borderline as far as practicality is concerned. In plant applications, filter permeability losses in the range of 80 to 90% would be considered acceptable, but in the extrapolation of test results, some allowance must also be made for additional permeability loss due to longer service time and exposure to a wider variety of dusts.

#### CONNECTORS

A connector was assembled to test the suitability of ASTM A-193-62T grade B-4 steel as flange bolt material for the ORNL fluoride volatility processing plant. Eight 5/8-inch bolts of this material were used to compress a 2-ring touchpoint soft nickel gasket between the two 150-pound, 4-inch Duranickel flat-faced flanges. A compressive loading, computed to be about 700,000 pounds, based on bolt elongation data, was applied to the assembly. The joint was then placed in an oven, buffered with 10 psig nitrogen, and successfully heat cycled between 100 and 370°C for ten complete cycles. The temperature was increased to 540°C, at which point the point seal failed. Considerable rust was observed on the bolts when the joint was disassembled; however, the nuts were removed without much difficulty.

It was concluded that Inconel-X, tested previously, might be somewhat more desirable as a bolt material than steel, because of the reasonable possibility that the rusting, which would take place with steel over a long operating period, could make nut removal extremely difficult.

#### PRODUCT PURIFICATION ON SORPTION-DESORPTION SYSTEM

Studies have been reported previously in which beds of sodium fluoride were used to absorb uranium from gas streams containing 10% uranium hexafluoride. Gases entered the top and flowed out the bottom of the bed which was contained in a 4-inch-diameter trap. Trap velocities were 0.08 and 0.19 ft/sec\*. A few runs were also made with feed streams which

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\* Smiley, S. H., Brater, D. C., and Pashley, J. H., ORGDP Fuel Reprocessing Studies Summary Progress Report Fiscal Year 1964 through Fiscal year 1965, Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, October 29, 1965 (K-1649), pp. 74-80; and Smiley, S. H., Brater, D. C., and Pashley, J. H., ORGDP Fuel Reprocessing Studies Summary Progress Report July through December, 1965, Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, June 28, 1966 (K-1669), pp. 48-49.

contained 500 ppm or less uranium hexafluoride to simulate situations where final polish-up of an exhaust stream is desirable from the viewpoints of economics and health\*.

Additional uranium hexafluoride sorption studies utilizing concentrations ranging from 2 to 3.7% uranium hexafluoride and a superficial gas velocity of 1 ft/sec have now been made in the 4-inch-diameter sodium fluoride sorption test loop. The trap was filled with 18 kg of sodium fluoride pellets prepared by heating 1/8-inch sodium bifluoride pellets to 540°C for 5 hours in an inert atmosphere. Basic operating conditions for the test were as follows:

Sorption Cycle:	Trap Temperature, °C	120
	Total Gas Flow, scfm	3.7
	Nominal Residence Time, seconds	7
Desorption Cycle:	Trap Temperature, °C	400
	Desorption Time, hours	14

Gas flows were maintained in a downward direction through the trap during sorption and then reversed during desorption. A small flow of nitrogen and fluorine was used during desorption to convey the liberated uranium hexafluoride to the cold traps and to reconvert any uranium pentafluoride produced by the high desorption temperature to uranium hexafluoride. Results of the series of sorption runs are shown in table XXVI.

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\* Smiley, S. H., Pashley, J. H., and Schappel, R. B., ORGDP Fuel Reprocessing Studies Summary Progress Report January through June, 1966, Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, January 18, 1967 (K-1691), p. 57.

TABLE XXVI

## RESULTS OF FIXED SODIUM FLUORIDE PELLET BED SORPTION TESTS\*

Run Number	Inlet UF <sub>6</sub> Concentration, %	Sorption Time, hr	UF <sub>6</sub> Sorbed, lb	Sorption Ratio, lb UF <sub>6</sub> /lb NaF
1	3.7	1.1	13.5	0.34
2	2.7	1.8	9.0	0.23
3	2.5	2.0	9.0	0.23
4	2.5	2.0	9.0	0.23
5	2.0	3.7	9.5	0.24
6	2.0	2.2	9.5	0.24
7	2.0	2.1	8.0	0.20
8	2.0	2.0	8.0	0.20
9	2.0	2.0	9.5	0.24
10	2.0	2.1	7.0	0.18

\* Superficial gas velocity = 1 ft/sec.

Outlet uranium hexafluoride concentrations during sorption were less than 50 ppm until breakthrough occurred. The sorption ratio (the pounds of uranium hexafluoride per pound of sodium fluoride at breakthrough) was higher in run 1, i.e., 0.34, than in any of the subsequent tests, 0.18 to 0.24, because the sorbent had not been previously loaded with uranium hexafluoride. Generally speaking, the sorption ratios obtained were about equal to those obtained in the earlier experiments with 10% uranium hexafluoride. These latest runs indicate that acceptable sorption capability can be attained with streams containing 2 to 4% uranium hexafluoride at the relatively higher superficial velocity of 1 ft/sec. The information is useful in evaluation of backup trap applications, particularly if sudden releases of diluted material may be encountered.

#### PERIPHERAL COMPRESSOR

A 2,000-hour operation target for the first peripheral compressor service test with fluorine was surpassed during the previous semiannual report period. After a total of 2,413 hours of operation, of which 2,016 hours was with mixtures of 20 to 75% fluorine in nitrogen, the compressor was removed from the pump loop and disassembled.

An inspection was made of all component parts with particular attention focused on evidences of fluorine attack. Upon removal of the impeller housing front plate, a very light, almost undetectable surface film was found on all surfaces. When this film was wiped away, the metal exposed to fluorine atmospheres during the testing appeared to have retained its as-installed luster although the outside of the impeller housing was somewhat discolored, apparently due to temperature effects. The nickel labyrinth seal between the two stages and the Duranickel impeller also exhibited good resistance to fluorine attack. The excellent condition of the impeller and the impeller housing are illustrated in figure 12, a photograph taken after the disassembly and wiping. The pits in the impeller and the minute scratches on both pieces are machine marks made during fabrication and balancing.

The rear motor bearing was found to be in good serviceable condition, although the grease was somewhat stiff but not caked.

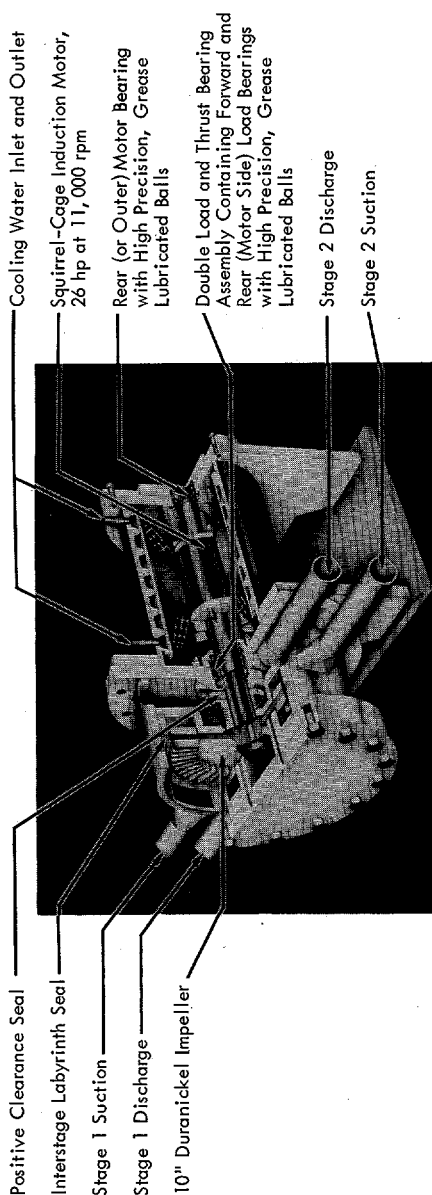
When the double load and thrust bearing assembly on the pump side of the motor was removed, both the forward (process side) and rear (motor side) bearing retainers were found covered with a thin layer of black, gritty grease. The forward retainer was easily wiped clean but not the rear retainer. The inside bores of both races were not discolored, indicating that the load bearing assembly had not overheated during the testing program, and that the 88°C cut-off is adequate to prevent damage because of high temperature. There was a minimum amount of grease packed behind and around the balls.

The forward ball bearing retainer ring was partially charred, while the rear retainer ring was rough and darkened. There were also cracks in both rings. These retainer rings are made of a phenolic type material. The balls in the forward load bearing were slightly scratched, while the balls in the rear load bearing were slightly discolored.

The front portion (process side) of the motor windings was covered with a film of very black, oily substance. A single bare segment of coil wire was found in one of the windings, and a small burned spot was found on the motor rotor. Apparently a short circuit had developed between the bare coil wire and the rotor. The motor was examined in the ORGDP electrical shop and found otherwise to be in satisfactory operating condition.

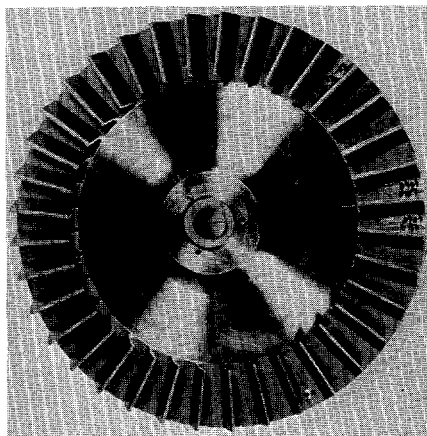
Generally speaking, the compressor was in good shape. The deterioration of the retainer rings can probably be ascribed to inadvertent exposures to fluorine early in the test when there was an insufficient supply of nitrogen to the shaft seal. Samples of the charred phenolic and the grease from load and rear bearings were found to contain 0.2, 6.1, and 2% fluorine, respectively. The fluorine may have burned the phenolic retainer ring of the forward load bearing, and pieces of the char probably flaked off. The pieces could have been abrasive enough to scratch the balls. Test loop instrumentation and the buffer systems have been reworked to minimize the possibility of reoccurrence of this difficulty.

PHOTO NO. PH-66-51



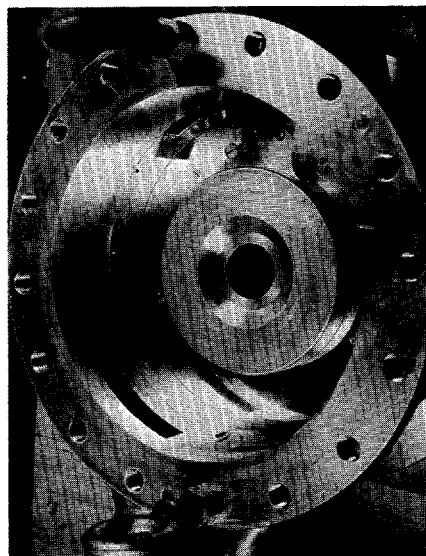
PERIPHERAL COMPRESSOR

PHOTO NO. PH-66-1791



10" DURANICKEL IMPELLER

PHOTO NO. PH-66-1793



IMPELLER HOUSING

PERIPHERAL COMPRESSOR SCHEMATIC AND EXPOSURE DETAILS

Figure 12

The compressor was reassembled with new bearings, and extended period testing was resumed. To date, 1,293 hours has been logged, including 855 with 5 to 60% fluorine in nitrogen and more than 100 with mixtures containing low concentrations of uranium hexafluoride and fluorine. Operation has been excellent.

With the compressor running at 9,100 rpm, load and rear bearing temperatures have remained steady at  $56 \pm 1^\circ\text{C}$  and  $43 \pm 1^\circ\text{C}$ , respectively. A suction pressure of 13.5 psia and a discharge pressure of 13.2 psig have been maintained. Electrical load requirements have been on the order of 5.2 kw.

A du Pont 400 photometric analyzer has been used to analyze for fluorine in the gas sampled from the high pressure side of the compressor. No problems were encountered with the instrument. The fluorine concentrations indicated by the instrument were compared with laboratory analyses of the gas stream, and the cross-check indicated that analyzer response was linear over the 5 to 60% fluorine concentration range.

#### FLUORINATION OF ARGONNE NATIONAL LABORATORY REACTOR BED MATERIAL

Nonirradiated volatility process reactor bed materials from ANL, runs BRF5-5 through -8, have been fluorinated with elemental fluorine in the ORGDP filter test loop. In the preparation of the material at ANL, charges of uranium dioxide and alumina had been processed through the oxidation and bromine pentafluoride fluorination steps under the conditions listed in table XXVII. Chemical decladding involving hydrochlorination was not employed in the preparation. The reactor was charged prior to the oxidation step with uranium dioxide pellets and simulated fission product compounds which amounted to approximately 7% of the total bed weight. The compounds are listed in table XXVIII. The product from the elemental fluorine treatment is to be used in ORNL waste processing studies.

The ORGDP fluorinations were conducted in the 4-inch-diameter filter loop reactor. The charge weights before and after the treatment are summarized as follows:

	ANL Run Number*			
	<u>BRF5-5</u>	<u>BRF5-6</u>	<u>BRF5-7</u>	<u>BRF5-8</u>
Batch Weight, g	6,537	2,946	3,388	6,238
Final Bed Weight, g	7,185	3,816	3,427	6,704
Weight Gain as the Result of Fluorination, g	648	871	39	466

\* Numbers correspond with ANL run numbers. There were no ORGDP run numbers 1 through 4 in this series.

TABLE XXVII  
ARGONNE OPERATING CONDITIONS\*

Run Number	Temperature, °C	Reagent Concentration, volume percent	Velocity at Operating Conditions, ft/sec	Uranium Dioxide Charge†, kg	Time, hr
Oxidation Step:					
BRF5-5	450	20	1.4	4.4	11
BRF5-6	450	20	1.4	2.2	6
BRF5-7	450	20	1.4	2.2	6
BRF5-8	450	20	1.4	4.4	11
Fluorination Steps:					
BRF5-5	225	12	0.6		6
BRF5-6	300	21	1.0		2
BRF5-7	225	20	0.6		3
BRF5-8	300	12	1.0		4

\* Holmes, J. T., Koppel, L. B., Saratchandran, N., Strand, J. B., and Ramaswami, D., Engineering Development of Fluid Bed Fluoride Volatility Processes, XIII, Pilot Plant Studies of the Fluorination of Uranium Oxide with Bromine Pentafluoride, Argonne National Laboratory, December, 1967 (ANL-7370).

† The bed diluent in all runs was 48 to 100 mesh alumina.

§ Bromine pentafluoride was used as the fluorinating agent.

TABLE XXVIII

FISSION PRODUCT COMPOUNDS ADDED BY ANL PRIOR TO OXIDATION STEP  
IN PREPARATION OF BED MATERIAL FOR ORNL STUDIES

<u>Compound</u>	<u>Amount, grams</u>			
	<u>Run</u> <u>BRF5-5</u>	<u>Run</u> <u>BRF5-6</u>	<u>Run</u> <u>BRF5-7</u>	<u>Run</u> <u>BRF5-8</u>
SeO <sub>2</sub>	0.54	0.27	0.27	0.54
SrF <sub>2</sub>	23.41	17.71	17.71	23.41
RbF	17.74	8.87	8.87	17.74
Y <sub>2</sub> O <sub>3</sub>	10.19	5.10	5.10	10.19
ZrO <sub>2</sub>	74.55	37.28	37.28	74.55
MoO <sub>3</sub>	79.74	39.87	39.87	79.74
RuO <sub>2</sub>	28.31	14.16	14.16	28.31
RhO	5.89	2.95	2.95	5.89
PdO	4.33	2.17	2.17	4.33
Ag <sub>2</sub> O	0.059	0.030	0.030	0.059
CdO	0.146	0.073	0.073	0.146
In <sub>2</sub> O	0.021	0.011	0.011	0.021
SnO <sub>2</sub>	0.21	0.11	0.11	0.21
Sb <sub>2</sub> O <sub>5</sub>	0.089	0.045	0.045	0.089
I	2.86	1.43	1.43	2.86
CsF	37.85	37.85	37.85	37.85
BaO	21.59	10.80	10.80	21.59
La <sub>2</sub> O <sub>3</sub>	18.21	9.11	9.11	18.21
CeO <sub>2</sub>	45.90	22.95	22.95	45.90
PrO <sub>4</sub>	21.74	10.37	10.37	21.74
Nd <sub>2</sub> O <sub>3</sub>	66.13	33.07	33.07	66.13
Sm <sub>2</sub> O <sub>3</sub>	12.31	6.11	6.11	12.31
Eu <sub>2</sub> O <sub>3</sub>	0.46	0.23	0.23	0.46
Gd <sub>2</sub> O <sub>3</sub>	0.81	0.09	0.09	0.18



As suggested by ANL, a fluorine concentration of 50%, a bed temperature of 550°C, and a superficial gas velocity of 0.5 ft/sec were employed for runs BRF5-5 and -6, thus simulating the most rigorous exposure condition in the plutonium volatilization step of the fluoride volatility process.

After the run BRF5-5 material was charged, the bed was fluidized with argon and heated to the 550°C temperature. When 50% fluorine in argon was admitted to the reactor, an immediate temperature excursion in excess of 50°C was noted, and the fluorine was subsequently valved out. Intermittent fluorine exposures, totaling about 30 minutes, were then conducted during the next 3 hours until the temperature excursions ceased. The material was then exposed to 50% fluorine at 550°C for an additional 7.5 hours; after which the bed was cooled to room temperature and was removed. Some caking or crusting was observed on the top of the bed and at a zone several inches below the top, with the layers separated by powder. These cakes were readily broken up with the vacuum nozzle used for the bed removal.

The second charge, run BRF5-6, weighed about one-half of that for run BRF5-5. Fluorination operating conditions were similar to those for the first run except that external cooling with steam was employed to limit reactor bed temperature increases to 50°C; however, when the bed material was removed, a nickel support grating in the bottom of the reactor exhibited signs of high temperature exposure. The bed caking appeared somewhat more severe than with the first material processed but was found chiefly at the bottom of the reactor in the vicinity of the bed support. These results indicated that both bromine pentafluoride exposures at ANL had failed to satisfy the total fluorine demand of the material in the beds.

Runs BRF5-7 and -8 fluorinations were initiated at low concentrations of fluorine. The concentrations were then increased slowly so that the reaction bed temperature rises were limited to 50°C. The final fluorine concentration in the gas feed was 50%. The material was then exposed to this gas concentration for 8 hours at 550°C. Very little bed caking was observed.

The weight gains with runs BRF5-7 and -8 material were less than one-half those experienced with runs BRF5-5 and -6 material. The results indicate that the reaction with bromine pentafluoride was more complete in the latter two ANL runs.